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Contents of Vol. XXVII.

No. 3.

No. 4.

REPORT.

No. 5.

REVIEWS.

No. 6.

REPORTS.

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METHYL DERIVATIVES OF INDIGO.

By M. Kuhara and M. Chikashigé.

I. GENERAL CONSIDERATIONS.

In our last article[1] it was shown that Flimm's[2] synthesis of indigo, which consists of the fusion of bromacetanilide with dry caustic potash, may satisfactorily be explained by assuming the formation of diphenyldiketopiperazine as an intermediate product, since, in fact, indigo can be formed from the latter as well as from bromacetanilide.

If our view be correct, those substituted brom- or chloracetanilides which are so constituted as not to be able to form the piperazine ring would not yield the substituted indigos. According to Flimm,[3] indigo is formed from bromacetanilide by molecular rearrangement, through the intermediate stage of pseudoindoxyl. Heumann[4] believed that phenylglycocoll bromide and then pseudoindoxyl are first formed. If this be true, a substituted brom- or chloracetanilide, such as methylchloracetanilide, ought to yield dimethylindigo in which the methyl groups have replaced the hydrogen atoms of the imido groups, as will be assumed :

[1] This Journal, **24**, 167.
[2] Ber. d. chem. Ges., **23**, 57.
[3] *Loc. cit.*
[4] *Ibid.*, **23**, 3045.

$$C_6H_5-N\underset{CO.CH_2Cl}{\overset{CH_3}{\big<}} \;\rightarrow\; C_6H_4\underset{\overset{|}{C}H_2}{\overset{N}{\big<}}\underset{CO}{\overset{CH_3}{\big>}} \;\rightarrow\;$$

$$C_6H_4\underset{CO}{\overset{N}{\big<}}\underset{CH_2}{\overset{CH_3}{\big>}} \;\rightarrow\; C_6H_4\underset{CO}{\overset{N}{\big<}}\overset{CH_3}{\big>}C=C\underset{CO}{\overset{N}{\big<}}\overset{CH_3}{\underset{C_6H_4,}{\big>}}$$

$$\text{or}\quad C_6H_5-N\underset{CO.CH_2Cl}{\overset{CH_3}{\big<}} \;\rightarrow\; C_6H_5-N\underset{CH_2.COCl}{\overset{CH_3}{\big<}} \;\rightarrow\;$$

$$C_6H_5.N\underset{CH_2.COOH}{\overset{CH_3}{\big<}} \;\rightarrow\; C_6H_4\underset{CO}{\overset{N}{\big<}}\underset{CH_2}{\overset{CH_3}{\big>}} \;\rightarrow\;$$

$$C_6H_4\underset{CO}{\overset{N}{\big<}}\overset{CH_3}{\big>}C=C\underset{CO}{\overset{N}{\big<}}\overset{CH_3}{\underset{C_6H_4.}{\big>}}$$
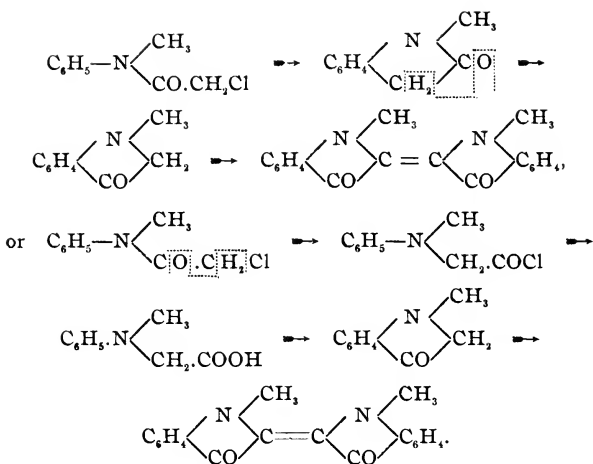
Now, in order to decide the points in question, the authors have specially prepared methylchloracetanilide,

$$C_6H_5-N(CH_3).CO.CH_2Cl,$$
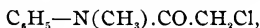
which is considered to be chloracetanilide in which the hydrogen of the imido group has been replaced by methyl, and hence it can not form the piperazine ring. It was then subjected to fusion with caustic potash and found to decompose entirely, not giving a trace of indigo derivatives. Its deportment towards the fused potash was apparently different from that of ordinary chloracetanilide. Flimm[1] also states that phenylchloracetanilide,

$$C_6H_5.N.C_6H_5.CO.CH_2Cl,$$
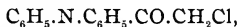
prepared from diphenylamine and chloracetyl chloride did not give phenyl derivatives of indigo at all under similar treatment. The authors repeated his experiments and obtained the same results, which must be due, as they believe, to the impossibility of the formation of the piperazine ring.

There is another fact which may support the author's view.

[1] *Loc cit.*

Hausdörfer[1] claims that he obtained phenylglycocoll by treating diphenyldiketopiperazine with alcoholic potash; we followed his method with diorthotolyldiketopiperazine and succeeded in getting a very small quantity of orthotolylglycocoll. Now we maintain that phenylglycocoll may be formed from diphenyldiketopiperazine by the action of fused caustic potash just as it is when alcoholic potash is used, and that indigo is formed by its further action.

On extending this principle to the formation of the derivatives of indigo, we succeeded in getting the different methyl derivatives. The experiments were conducted with chloracetyl derivatives of ortho, meta- and paratoluidines as well as with diortho- and diparatolyldiketopiperazines, dimethylindigo being obtained in each case. And also with chloracet-*unsym.*-metaxylide and chloracetpseudocumidide, and with their corresponding diaryldiketopiperazines, tetra- and hexamethylindigos were obtained.

For designating the positions of methyl groups in different methyl indigos, we propose to number the carbon atoms in the two benzene nuclei of indigo, as shown in the following formula :
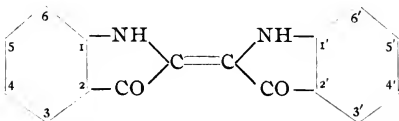
As only one dimethylindigo is possible from either diorthotolyldiketopiperazine (or chloracetorthotoluide) or diparatolyldiketopiperazine (or chloracetparatoluide), we believe that the dimethylindigo from the former has the structure
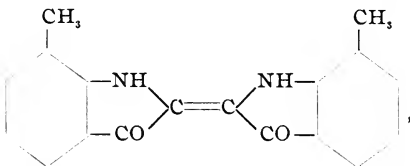
[1] Ber. d. chem. Ges., **22**, 1802.

and we call it 6.6'-dimethyl indigo, while from the latter we get

CH₃—⟨ring⟩—NH / —CO ⟩C = C⟨ NH— / CO— ⟨ring⟩—CH₃ ,
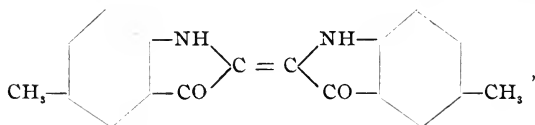
which is 4.4' dimethylindigo.

Three isomeric forms are possible from dimetatolyldiketo-piperazine (or chloracetmetatoluide) :

I.

CH₃—⟨ring⟩—NH / —CO ⟩C = C⟨ NH— / CO— ⟨ring⟩—CH₃

5.5'-Dimethylindigo.

II.

⟨ring⟩—NH / —CO ⟩C = C⟨ NH— / CO— ⟨ring⟩
ĊH₃　　　　　　　　　　　　　　ĊH₃

3.3'-Dimethylindigo.

III.

CH₃—⟨ring⟩—NH / —CO ⟩C = C⟨ NH— / CO— ⟨ring⟩
　　　　　　　　　　　　　　　　　　ĊH₃
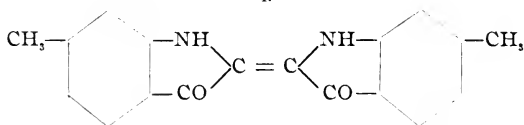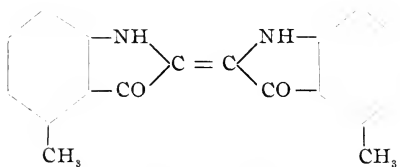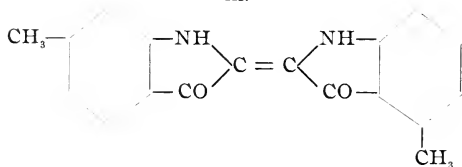
5.3'-Dimethylindigo.

We must decide which of these three formulas corresponds to the dimethylindigo obtained by us from chloracetmeta-toluide. Based upon the rules of orientation universally ac-cepted, the CO group enters the para position, with reference

to the CH$_3$ group, more readily than the ortho position, and hence the dimethylindigo of the formula (I.), or 5.5′-dimethylindigo, may be the principal product of the reaction.

Tetra- and hexamethylindigos, formed respectively from di-*unsym.*-metaxylyldiketopiperazine or chloracet-*unsym.*-metaxylide, and dipseudocumyldiketopiperazine, or chloracet-pseudocumidide, must evidently possess the following structures:

4.6,4′.6′-Tetramethylindigo.

3.4.6,3′.4′.6′-Hexamethylindigo.
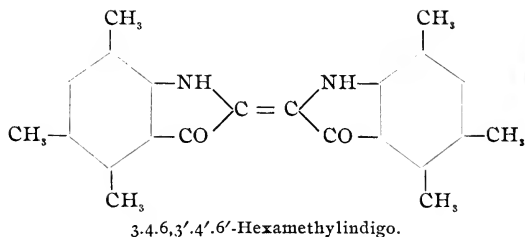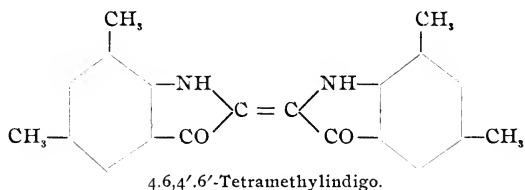
On referring to the literature, we find the different methyl derivatives of indigo which are already known. Dimethylindigo obtained by Flimm[1] from bromacetparatoluide, and by Eckenroth[2] from chloracetparatoluide, the so-called *p*-dimethylindigo, lately prepared by Kunckell[3] from *p*-methyl-*o*-acetylamidochloracetophenone, and 4.4′-dimethylindigo made by the authors from diparatolyldiketopiperazine are all identical. So-called metamethylindigo[4] was also prepared at Farbewerke vorm. Meister, Lucius and Brüning from ortho-nitrometamethylbenzaldehyde, but its constitution is quite

1 Ber. d. chem. Ges., **23,** 59.
2 *Ibid.*, **24,** 693.
3 *Ibid.*, **33,** 2648.
4 *Ibid.*, **16,** 817 (Ber. ii. Pat.).

obscure, because, though it should be identical with either 4.4'- or 6.6'-dimethylindigo, interpreting its formation from the theoretical standpoint, it shows an entirely different spectrum from either of the other two, and consequently must possess a different structure. Flimm once tried to get an isomeric dimethylindigo from chloracetorthotoluide by the potash fusion, but, having been unsuccessful, he ascribes the failure to the presence of one of the ortho positions previously occupied by a methyl group. But the substance, like indigo, obtained from orthotolylglycocoll by the potash fusion at the Badische Anilin- und Soda-Fabrik[1] may be identical with our 6.6'-dimethylindigo prepared from diorthotolyldiketopiperazine or chloracetorthotoluide. And an indigo derivative obtained also at the Badische Anilin- und Soda-Fabrik[2] from metaxylylglycocoll and 4.6,4'.6'-tetramethylindigo obtained by us from di-*unsym.*-metaxylyldiketopiperazine or chloracet-*unsym.*-metaxylide, may possibly be identical.

Besides the formation of indigo or its methyl derivatives, as the principal reactions, from diphenyldiketopiperazine or ditolyldiketopiperazines, we have observed the production of phenylisonitril, potassium carbonate, and primary and secondary amines, just as in the case of Heumann's synthesis. We thus have further proof that diaryldiketopiperazine may break down into arylglycocoll, which, in turn, would undergo changes as in Heumann's process.

II. METHYLCHLORACETANILIDE,

$$C_6H_5-N\Big\langle{}^{CH_3}_{CO.CH_2Cl}.$$
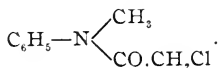
This substance has not been known hitherto. At first methylaniline was prepared according to Hepp's[3] method. On mixing it with chloracetyl chloride, each in well-cooled ethereal solution, methylchloracetanilide was obtained in the form of a crystalline powder. It crystallizes from hot water, on cooling, in the form of fine needles, but sometimes in large

[1] Ber. d. chem. Ges., **25**, Ref. 488 (Ber. ü Pat.).

[2] *Loc. cit.*

[3] Ber. d. chem. Ges., **10**, 327.

prisms from its dilute solution. It sublimes when heated and attacks the skin to some extent. The melting-point of the crystals is 61°. The crystals dried between the folds of filter-paper, or kept in a desiccator for a few days, gave, on analysis, the following results :

I. 0.4374 gram substance gave 0.0813 gram Cl.

II. 0.4998 gram substance gave 0.0919 gram Cl.

	Calculated for $(ClCH_2.CO.N.CH_3.C_6H_5)_2.H_2O$.	I.	Found. II.
Cl	18.44	18.59	18.39

After the crystals had been kept in a desiccator for more than a week they were again analyzed.

0.1721 gram substance gave 0.0332 gram Cl.

	Calculated for $ClCH_2.CO.N.CH_3.C_6H_5$.	Found.
Cl	19.35	19.29

Methylchloracetanilide, when fused with caustic potash, behaves quite differently from chloracetanilide or chloracettoluide. It never yields substances related to indigo but decomposes entirely.

III. DIMETHYLINDIGOS.

The chloracetorthotoluide used in the experiments was prepared according to the directions given by Abenius and Widman,[1] whose process consists in mixing 1 molecule chloracetyl chloride with 2 molecules orthotoluidine, each in well cooled ethereal solution. P. Meyer[2] recommends benzene as a solvent instead of ether. We have, however, found it more advantageous, as we believe, to use the ethereal solutions of the two substances cooled with ice, so as to give the theoretical yield of the product.

Chloracetmetatoluide has not been described in the literature hitherto. For its preparation exactly the same process as above given was used. The substance was purified by repeated recrystallization from hot water and dried over calcium chloride, and its chlorine was determined.

[1] J. prakt. Chem. [2], **38**, 299.

[2] Ber. d. chem. Ges., **8**, 1154.

I. 0.2510 gram substance gave 0.0481 gram Cl.
II. 0.2162 gram substance gave 0.0411 gram Cl.

	Calculated for $CH_3.C_6H_4.NH.CO.CH_2Cl.$	Found. I.	II.
Cl	19.35	19.17	19.05

It melts at 141°. It is somewhat volatile, even at ordinary temperatures, and sublimes when heated. Its property of attacking the skin, its solubility, and other properties are similar to those of the orthotoluide.

Chloracetparatoluide was prepared by Tommasi,[1] by Eckenroth and Donner,[2] and by Meyer.[3] It was also prepared in the same way as the isomeric toluides.

From chloracetorthotoluide and chloracetparatoluide diortho- and diparatolyldiketopiperazines were prepared, respectively, by the process suggested by Abenius.[4] We were, however, not able to get dimetatolyldiketopiperazine, since only a few grams of chloracetmetatoluide were at hand. These diaryldiketopiperazines readily yield dimethylindigos.

1. 6.6'-Dimethylindigo,
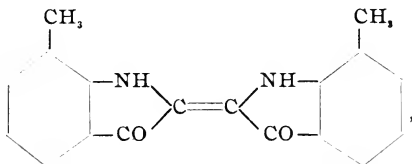
was easily formed from diorthotolyldiketopiperazine as well as from chloracetorthotoluide by fusing with caustic potash.

Flimm states that he failed to get dimethylindigo from chloracetorthotoluide by fusing with caustic potash, but, on the contrary, we found that it could be formed from chloracetorthotoluide, and also from its corresponding ditolyldiketopiperazine, with a tolerably good yield. We mixed chloracetorthotoluide with an equal volume of dry powdered caustic potash, and heated the mixture in a test-tube or flask.

[1] Bull. soc. chim., **19**, 400.
[2] Ber. d. chem. Ges., **23**, 3257.
[3] *Ibid.*, **8**, 1154.
[4] *Ibid.*, **21**, 1665.

The mixture instantly assumed a reddish-yellow color, when the potash began to fuse, then turned pale-yellow and reddish-brown, and finally changed to greenish-yellow on cooling. The mass was now treated with water, and from the solution dimethylindigo precipitated immediately on exposure to the air. Its production was shown to be dependent wholly upon the nature of the caustic potash used. When containing potassium carbonate, it was found to give the best result, and after several trials the following proportions of the materials were found to be most favorable :

Chloracetorthotoluide	100 parts
Dry powdered caustic potash	175 "
Potassium carbonate	25 "

Without mixing any potassium carbonate intentionally the yield of the dimethylindigo was very poor or often none. Its action is, however, not quite certain, but its presence may probably keep the mixture from being entirely fused when heated, thus avoiding the free access of air, and also preventing too violent an action of the potash which would, in that case, be destructive. The use of a glass vessel should be avoided for the fusion, since it is rapidly corroded by the melted potash. Thus a nickel crucible was substituted with the following precautions : A square box of asbestos-board, having a hole at its bottom just large enough to allow the crucible to rest over it, was constructed, and a cover of the same material was made to fit. A gas flame was applied from below, so as to heat directly the bottom of the crucible. We at first thought it best to pass nitrogen gas into the box in order to prevent the oxidation of the product, but soon found it unnecessary to do so in consequence of the evolution of heavy vapors which fill the box and exclude air. The reactions proceed smoothly.

For the purification of the dimethylindigo so obtained several methods were tried, and at last we found it most advantageous to filter the precipitate of dimethylindigo and to wash successively with hot water and alcohol, the latter completely dissolving out the resinous matter. For analysis we had to sublime it under 35 to 40 mm. pressure, according to

Sommaruga.[1] The sublimate was again washed with alcohol and ether to get rid of heavy hydrocarbons which may possibly have been formed by the decomposition of the dimethylindigo. Precipitated dimethylindigo can also be purified by washing with alcohol, then dissolving in hot chloroform, and removing the residue from the solution. This process is most convenient for purifying from silica which is derived from the glass vessels used.

Sublimed dimethylindigo was analyzed by Dumas' method.

I. 0.3158 gram substance gave 25.7 cc. nitrogen at 14° C. and 756.7 mm. pressure.

II. 0.2158 gram substance gave 17.9 cc. nitrogen at 20° C. and 756.4 mm. pressure.

	Calculated for $CH_3.C_6H_3\diagup\overset{CO}{\underset{NH}{\diagdown}}C:C\diagup\overset{CO}{\underset{NH}{\diagdown}}C_6H_3.CH_3.$	Found.	
		I.	II.
N	9.66	9.53	9.47

6.6'-Dimethylindigo is a powder when precipitated but, when sublimed, it crystallizes in prisms very closely resembling ordinary indigo in appearance. It gives a bright violet vapor with partial decomposition when heated. Its characteristic property is its solubility in various solvents. One gram of the substance is soluble in about 2000 cc. alcohol and in 500 cc. chloroform. It is more or less soluble in ether, aniline, benzene, nitrobenzene, oil of turpentine, fused chloralhydrate, paraffin, linseed oil, acetic acid, and fuming sulphuric acid, and is, in general, more soluble than ordinary indigo. The colors of the solutions in these solvents vary from reddish-violet to green or blue. We observed the absorption band of the chloroform solution according to the statements of Krüss and Oeconomides,[2] seeking for the position of maximum darkness. When the solution is highly concentrated or its layer is thick, the absorption takes place from orange to green, while with ordinary indigo the range is much less. The results of our observations are given at the end of the paper.

[1] Ber. d. chem. Ges., **11**, 1355.
[2] *Ibid.*, **16**, 2051.

In order to examine the products of the secondary reactions, we collected the fumes evolved during the fusion by passing them into a vessel containing water. Oily drops suspended in water were found to be orthotoluidine and methylorthotoluidine.

It is unnecessary to describe the fusion of diorthotolyldiketopiperazine here, because its behavior toward caustic potash is precisely the same as that of chloracetorthotoluide. The dimethylindigo formed agrees in all respects with that from chloracetorthotoluide.

2. 5.5′-Dimethylindigo,

$$CH_3 - \bigcirc - NH \diagdown C = C \diagup NH - \bigcirc - CH_3,$$
$$\qquad - CO \diagup \qquad \diagdown CO -$$
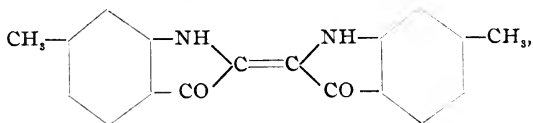
was formed from chloracetmetatoluide by the same method as its isomers, but the conditions of fusion were apparently different from the former cases. It seems strange that in this case the addition of potassium carbonate to the caustic potash was of no benefit; this may, however, be due to the high melting-point of dimetatolyldiketopiperazine which is formed as an intermediate product in the reaction. Although we could not prepare it, as the quantity of chloracetmetatoluide at hand was very small, yet we infer that its melting-point may be higher than that of the ortho compound, as will be seen from the following data:

	Melting-point.
Chloracetorthotoluide	111° to 112°
Chloracetmetatoluide	141°
Chloracetparatoluide	161°.5
Diorthotolyldiketopiperazine	159° to 160°
Dimetatolyldiketopiperazine	....
Diparatolyldiketopiperazine	252° to 253°

5.5′-Dimethylindigo resembles its isomers in its properties. It is soluble in alcohol, ether, chloroform, etc. Its solubility in chloroform is about 1 : 1000. It differs somewhat from its

isomers in the absorption band, as will be seen from the annexed table.

3. 4.4'-Dimethylindigo,
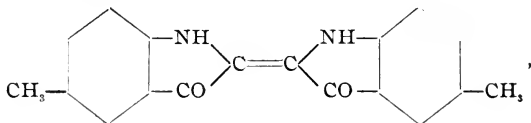
was formed from diparatolyldiketopiperazine and also from chloracetparatoluide under the same conditions as the meta compound. Ir was found to be identical with the dimethylindigo already known, as explained in the preceding part of the paper. Its solubility in chloroform is almost the same as that of 5.5'-dimethylindigo.

IV. TETRAMETHYLINDIGO.

4.6,4'.6'-Tetramethylindigo,
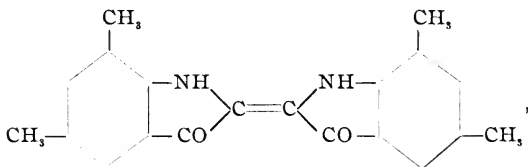
was formed from chloracet-*unsym.*-metaxylide and from di-*unsym.*-metaxyldiketopiperazine by fusing with caustic potash. Its properties are similar, in many respects, to those of the other methyl derivatives of indigo. Its solubilities and the position of the absorption band are given in the table below.

Chloracet-*unsym.*-metaxylide was prepared by mixing 100 grams of *unsym.*-metaxylidine and 50 grams of chloracetyl chloride, each dissolved in benzene. The yield was almost theoretical. It crystallizes in silky needles from benzene, and does not attack the skin. Its melting-point is 143°. The substance was analyzed with the following results:

I. 0.1141 gram substance gave 0.0204 gram Cl.

II. 0.1532 gram substance gave 0.0274 gram Cl.

	Calculated for $ClCH_2.CO.NH.C_6H_3(CH_3)_2$.	Found.	
		I.	II.
Cl	17.97	17.88	17.92

It produced di-*unsym.*-metaxlyldiketopiperazine by treating with alcoholic potash, as in the preparation of other diaryldiketopiperazines. It crystallizes in colorless needles and melts at 170°.

V. HEXAMETHYLINDIGO.

Chloracetpseudocumidide was prepared from pseudocumidine and chloracetyl chloride. It crystallizes in needles and melts at 158°.5. Its analytical results are as follows:

	Calculated for $Cl.CH_2.CO.NH.C_6H_2(CH_3)_3$.	Found.
Cl	16.79	17.00

Dipseudocumyldiketopiperazine formed from the above substance crystallizes in colorless needles and melts at 221°.5.

A corresponding methyl derivative of indigo, or 3.4.6, 3'.4'.6'.-hexamethylindigo,
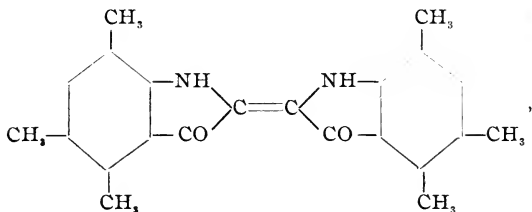
was obtained from chloracetpseudocumidide as well as from dipseudocumyldiketopiperazine, but only in small quantity.

Positions of the Maximum Darkness in the Absorption Bands of the Methylindigos.   (*Chloroform Solution.*)

Name.	λ_1.	λ_2.	$\frac{\lambda_1 + \lambda_2}{2}$.
Ordinary indigo	622.7	587.6	605.1[1]
6.6'-Dimethylindigo	643.6	615.7	629.7
5.5'-Dimethylindigo	619.2	598.1	608.6
4.4'-Dimethylindigo	643.7	622.7	633.2
4.6,4'.6'-Tetramethylindigo	662.7	631.7	647.2

[1] Krüss and Oeconomides give $\frac{\lambda_1 + \lambda_2}{2} = 604.8$ for ordinary indigo.

Solubilities of the Methylindigos in Various Solvents.

Solvents.	Ordinary indigo.	6,6'-Dimethylindigo.	5,5'-Dimethylindigo.	4,4'-Dimethylindigo.	4,6,4',6'-Tetramethylindigo.
Alcohol	Insoluble	Soluble in cold; easily in hot with deep-blue color	Soluble with blue color	Soluble with blue color	Soluble with blue color
Ether	Insoluble	Soluble in cold with violet color	Sol'ble with reddish-violet color	Soluble with blue color	Less soluble with blue color
Chloroform	Slightly soluble with violet color	Easily soluble with violet color	Readily soluble with reddish-blue color	Readily soluble with blue color	Easily soluble with deep-blue color
Aniline	Slightly soluble in hot with bluish-green color	Soluble in cold with bluish-green color	Soluble with greenish-blue color	Soluble with green color	Soluble with green color
Nitrobenzene	Insol'ble in cold; soluble in hot with violet color	Difficultly soluble in cold, readily in hot with violet color	Soluble with green color	Slightly soluble with green color	Soluble with green color
Turpentine oil	Ins'l'ble in cold; slightly soluble in hot, but soon decolorizes	Slightly soluble in cold, more so in hot, but soon decolorizes	Soluble with blue color (slightly reddish) but soon decolorizes	S'l'ble, but soon decolorizes	Soluble with light-blue color but soon decolorizes

Solubility of the Methylindigos in Various Solvents (Continued).

Solvents.	Ordinary indigo.	6.6'-Dimethylindigo.	5.5'-Dimethylindigo.	4.4'-Dimethylindigo.	4,6,4',6'-Tetramethylindigo.
Chloral hydrate (melt'd)	Soluble with deep-blue color	Readily soluble with greenish-blue color	Soluble with dark-blue color	Readily soluble with bright-blue color	Moderately soluble with greenish-blue color
Paraffin (melt'd)	Slightly soluble with amethyst color	Sol'ble with violet color	Soluble with bright-violet color	Soluble with blue color	Sol'ble with violet color
Linseed oil	Sol'ble with violet color	S'l'ble with reddish-violet color	Soluble with reddish-blue color	Soluble with green color	Soluble with greenish-blue color
Acetic acid	Ins'l'ble in cold; slightly soluble in hot with blue color	Difficultly soluble in cold, readily in hot with blue color	Soluble with bright-blue col'r	Soluble with blue color	Soluble with blue color
Benzene	Slightly soluble in hot with amethyst color	Soluble in cold, readily in hot with violet color	Soluble with reddish-blue color	Soluble with blue color	Soluble with bluish-violet color

THE MOLECULAR WEIGHTS OF CERTAIN SALTS IN ACETONE.

BY HARRY C. JONES.

Dutoit and Friderich[1] stated, in 1898, that "we have found by the boiling-point method that the following salts, NH_4CNS, $HgCl_2$, NaI, LiCl, CdI_2, dissolved in acetone have the normal molecular weights." They do not give any data, but state that their results will be published later. An examination of the literature up to the present fails to show that any such results have been published thus far.

A year later this work was cited by Kahlenberg and Lincoln,[2] who pointed out that such solutions conduct the current to a considerable degree.

Facts such as these are of special interest to-day in the light of the modern theory of solutions. If a salt dissolved in any solvent should give a normal molecular weight over a wide range of dilution, and at the same time show a large molecular conductivity which would increase with the dilution, it would, indeed, be awkward for the theory of electrolytic dissociation in its present form. However, before amending or supplementing a theory, which has correlated hundreds of apparently isolated facts, and which has probably done more towards placing chemistry upon an exact basis than any other theory which has ever been proposed, it is necessary to examine very carefully the experimental evidence bearing upon it.

Since Dutoit and Friderich have given no account of the experiments, and have not even published the data upon which their conclusion is based, I determined to study the molecular weights of some of the above substances in acetone, by means of my[3] modification of the boiling-point method of Beckmann. I proposed to determine the molecular weight at various dilutions, to see whether a normal molecular weight

[1] Bull. soc. chim. [3]. 19, 334.

[2] J. Phys. Chem., 3, 32.

[3] This JOURNAL, 19, 581 ; Ztschr. phys. Chem., 31, 119.

would be obtained at any dilution, and if so, whether it would be obtained over a considerable range of dilution.

Before we can determine the molecular weight of any substance in any solvent it is necessary to know accurately the boiling-point constant of the solvent. The constant for acetone is given by Biltz[1] as 17.1. It, however, seemed desirable that this should be redetermined.

The acetone which I used in this work was a very pure sample, which was carefully freed from water. Its boiling-point, under normal pressure, was 56°.2 to 56°.4.

Boiling-Point Constant of Acetone.

In order to determine the boiling-point constant of a solvent it is necessary to select a substance which will not be dissociated by the solvent, and which will not act chemically upon it. It is also desirable that the dissolved substance should not have a very large molecular weight, in order that the rise in boiling-point should be fairly large. Naphthalene was selected as the dissolved substance since it fulfilled these conditions, and, further, could be obtained in a high degree of purity. Four determinations of the boiling-point constant of naphthalene were made, and the results are given below :

Acetone. Grams.	Naphthalene. Grams.	Rise in boiling-point.	Constant.
55.388	1.9591	0°.480	1737
55.494	2.0465	0°.495	1718
53.698	2.6866	0°.668	1709
52.818	2.5388	0°.652	1736
		Mean,	1725

The constant for acetone is taken as the mean of the above four values, and 1725 is used in all the following calculations:

Molecular Weight of Cadmium Iodide in Acetone.

Eight determinations of the molecular weight of cadmium iodide in acetone were made, at dilutions ranging from less than 0.1 to more than 0.4 normal. The results, in the order of increasing concentration, are given below :

[1] "Practical Method for Determining Molecular Weights," p. 179.

Acetone. Grams.	CdI_2. Grams.	Grams CdI_2 in 1000 grams solvent.	Conc. normal.	Rise in boiling-point.	Molecular weight.
55.158	1.7789	32.251	0.0881	$0°.124$	448.6
56.031	2.0540	36.658	0.1002	$0°.140$	451.7
57.5065	2.4951	43.388	0.1186	$0°.160$	467.8
57.5065	3.7259	64.799	0.177	$0°.234$	477.7
56.369	3.7790	67.040	0.183	$0°.236$	490.1
55.923	4.5020	80.503	0.220	$0°.282$	492.4
57.283	5.4000	94.269	0.2576	$0°.330$	492.9
57.283	8.5460	149.189	0.4076	$0°.504$	510.7

These results show, in the first place, that the molecular weight of cadmium iodide in acetone is not normal for any of the above dilutions. It does not even approach the value 366, which corresponds to the formula CdI_2. They show, further, that the molecular weight is not a constant, but varies with the dilution used. The range of the dilutions studied is about as great as was possible by the boiling-point method. More concentrated solutions were not employed because the laws of dilute solutions do not hold at great concentrations. It would have been of interest to study more dilute solutions to see how far the molecular weight would have decreased, and whether it would have approached the normal value and have remained constant as the dilution was still further increased; but it is obvious that the rise in boiling-point would be too small to measure.

The facts then show that the molecules of cadmium iodide are polymerized to a very considerable extent in acetone, even in the most dilute solutions which were used, the complex molecules gradually breaking down into simpler molecules as the dilution is increased. But Dutoit and Aston[1] found that cadmium iodide in acetone had an appreciable conductivity. They give the following values:

Cadmium iodide	v	4	8	16	32	64	128	256
	μ_v	10.4	11.7	11.4	11.5	11.6	11.9	12.0

The conductivity is not large, and we should not expect it to be very great, since the conductivity of cadmium iodide in water is abnormally small. These conductivity values are

[1] Compt. rend., **125**, 242.

not at all at variance with the large molecular weight found since there are many cases known where we have ionization and polymerization present in the same solution. The amount of the cadmium iodide dissociated into ions is, from the above figures, not large.

Molecular Weight of Ammonium Sulphocyanate in Acetone.

Six determinations of the molecular weight of ammonium sulphocyanate in acetone, over a considerable range of dilution, gave the following results :

Acetone. Grams.	NH_4CNS. Grams.	Grams salt in 1000 grams solvent.	Conc. normal.	Rise in boiling-point.	Molecular weight.
55.647	1.1143	20.0244	0.263	0°.392	88.1
53.529	1.1082	20.7028	0.271	0°.400	89.3
52.927	1.6251	30.7046	0.403	0°.535	98.6
53.529	2.5218	47.1109	0.618	0°.800	101.6
52.861	2.5907	49.0097	0.643	0°.840	100.6
52.927	2.7489	51.9376	0.681	0°.882	101.6

These results are analogous to those obtained with cadmium iodide. The molecular weight found is always higher than the normal, which is 76.2. The molecular weight is not a constant, but increases with the concentration. The molecules of ammonium sulphocyanate in acetone are, therefore, polymerized, the amount of polymerization increasing with the concentration, as is generally the case. As the dilution of the solution is increased the molecular complexes break down more and more into simple molecules, and at very great dilution it is probable that only a very few complex molecules would exist.

That solutions of ammonium sulphocyanate in acetone have some conductivity is shown by Laszczynski.[1] He gives the following results :

$$\text{Ammonium} \atop \text{sulphocyanate} \Bigg\} \begin{array}{cccccc} v & 1.45 & 2.90 & 5.8 & 11.6 & 23.2 \\ \mu_v & 14.6 & 16.3 & 18.5 & 21.6 & 25.6 \end{array}$$

The conductivity of this salt is larger than that of cadmium iodide, as would be expected. We have here also polymerization and dissociation in the same solution.

[1] Ztschr. Elektrochem., **2**, 56.

Molecular Weight of Mercuric Chloride in Acetone.

Two determinations were made at different dilutions, with the following results :

Acetone. Grams.	HgCl₂. Grams.	Grams HgCl₂ in 1000 grams acetone.	Conc. normal.	Rise in boiling-point.	Molecular weight.
53.320	5.953	111.647	0.412	$0^{\circ}.710$	271.2
52.309	3.6554	69.881	0.258	$0^{\circ}.450$	267.9

The molecular weight found agrees closely with that calculated for the formula $HgCl_2$, which is 271.2, and this value does not change appreciably with the dilution. It is obvious that the condition of this salt in solution is very different from the two already considered. There is no sign of polymerization of the molecules, and, consequently, no molecular complexes to break down as the dilution is increased. The molecules of mercuric chloride exist, then, in solution in acetone in the simplest possible state.

The question as to whether solutions of mercuric chloride in acetone conduct the current, is of special interest in the light of the above facts. It would be very remarkable, indeed, for a salt to give normal molecular weight which did not change with the dilution, and have any marked power of conducting the current.

We could say at once that it is highly improbable that mercuric chloride in acetone should have any considerable conductivity, since mercuric chloride in water—the strongest dissociating solvent—conducts to only a slight extent. But we are fortunate in having the data bearing upon this subject. Laszczynski[1] has measured the conductivity of mercuric chloride in acetone, and gives the following results :

Mercuric chloride	v	2.26	4.52	9.04	18.08	36.16
	μ_v	0.075	0.149	0.279	0.476	0.734

The conductivity is, thus, exceedingly small, just as would be expected.

Molecular Weight of Sodium Iodide in Acetone.

Five determinations of the molecular weight of sodium

[1] *Loc. cit.*

iodide in acetone, at very different dilutions, gave the following results :

Acetone. Grams.	NaI. Grams.	Grams NaI in 1000 grams acetone.	Conc. normal.	Rise in boiling-point.	Molecular weight.
51.876	0.921	17.754	0.118	0°.230	133.2
54.808	1.332	24.303	0.162	0°.304	137.9
51.287	1.5357	29.941	0.200	0°.371	139.2
55.088	2.0210	36.687	0.245	0°.440	143.8
51.876	2.3653	45.595	0.304	0°.550	143.0

The molecular weight of sodium iodide is not normal (149.9) at any of the dilutions employed. It is less than normal even in the most concentrated solution employed, and gradually diminishes as the dilution of the solution becomes greater and greater. This substance differs from the first two studied in that its molecular weight is always less than the normal, while in the cases of cadmium iodide and ammonium sulphocyanate the molecular weight found was always greater than the normal.

It is impossible to say at present what the conductivity of sodium iodide in acetone is, at the above dilutions. The conductivity of sodium iodide in acetone at much greater dilutions has been measured by Carrara.[1] It was found to be quite large, and increased rapidly with increase in dilution. At a volume of 256, the most concentrated solution whose conductivity was measured, the molecular conductivity is 126.3, while at a volume of 512, the molecular conductivity is 133.5. From these data the molecular conductivity at a volume of 10, would be somewhat less than 100. We propose to measure the conductivity of sodium iodide in acetone at greater concentrations, in connection with an investigation now in progress in this laboratory. For the present we can only say that it is very probable that sodium iodide also represents a condition in which there is both polymerization and dissociation.

It should be stated in connection with the work with sodium iodide, that the solutions in acetone were colored deeply yellow. I supposed at first that this was due to the liberation of iodine, but a test with starch paste showed that no free iodine

[1] *Gazz. chim. ital.*, **27**, I, 213.

was present.   The yellow color may be due to some reaction
between the acetone and sodium iodide, and I am inclined to
lay less stress upon these results than upon those with the
other three compounds.

I intended to determine also the molecular weight of lith-
ium chloride in acetone, but found that it was not sufficiently
soluble for the purpose.

Of the five substances which Dutoit and Friderich claim to
give normal molecular weights in acetone, I have studied four,
and find that only one gives any approach to normal values
over a considerable range of dilution, and this one, mercuric
chloride, has practically no conductivity.   The fifth substance
I could not investigate on account of its small solubility.
These substances, instead of presenting any exception to the
theory of electrolytic dissociation, fall directly in line with the
theory, as so many similar cases have done.   Indeed, it is
extremely interesting to see how many apparent exceptions to
the theory of electrolytic dissociation disappear as experimen-
tal methods become more refined, and experimental work
more accurately carried out.   The amount of evidence for the
general correctness of this most fruitful generalization is at
present so large that any apparent exception will be accepted
only after it has been very thoroughly substantiated by re-
peated experiments.   This should, however, not debar one
from trying to discover exceptions, since there is more interest
in one well-established exception than in many facts which
could all have been predicted before any work was done.

Further work along the line indicated by this paper will be
continued in this laboratory.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIV.,
May, 1901.

THE LOWERING OF THE FREEZING-POINT OF AQUEOUS HYDROGEN DIOXIDE.

BY HARRY C. JONES, JAMES BARNES, AND EDWARD P. HYDE.

A number of attempts have been made to find a solvent
whose dissociating power was greater than that of water.   A
large number of solvents have been studied in this connection

with the result that of all the liquids investigated, water has the maximum ionizing power.

After examining all the work[1] which has been done it appeared to us not improbable that hydrogen dioxide might have a higher dissociating power than water.   J. J. Thomson[2] pointed out some time ago that in terms of the theory of electrolytic dissociation a relation should exist between the dissociating power of solvents and their dielectric constants.   A similar relation was recognized a little later by Nernst.[3]   The dielectric constant of a mixture of hydrogen dioxide and water has been determined recently by Calvert.[4]   From this he has calculated the dielectric constant of pure hydrogen dioxide to be 92.8 at 18°, while the dielectric constant of water at the same temperature is 81.

That hydrogen dioxide should have a high dissociating power was suspected by Brühl[5] a number of years ago.   He regards the constitution of hydrogen dioxide to be

$$H-O\equiv O-H.$$

It is, therefore, in a high degree, an unsaturated compound, and since, according to Brühl, dissociating power depends upon the presence of tetravalent oxygen—upon the unsaturated condition—hydrogen dioxide should have a very high ionizing power.   Brühl expressed the opinion that if the dissociating power of hydrogen dioxide could be measured it would probably be found to be greater than that of water.

We undertook this work with the hope of being able to determine, directly or indirectly, the dissociating power of hydrogen dioxide.

Purification of Hydrogen Dioxide.

We at first attempted to purify hydrogen dioxide by the method described by Bredig and von Berneck.[6]   Marchand's commercial hydrogen dioxide was distilled on a water-bath

[1] A summary by H. C. Jones. This JOURNAL, **25**, 232.
[2] Phil. Mag., **36**, 320.
[3] Ztschr. phys. Chem., **13**, 531.
[4] Ann. der Phys., **1**, 483.
[5] Ber. d. chem. Ges., **28**, 2868.
[6] Ztschr. phys. Chem., **31**, 271.

under a pressure of about 80 mm. of mercury, until a very small residue remained. Pure barium hydroxide was added to the distillate until it was slightly alkaline, and then pure carbon dioxide was run into the solution to convert the excess of barium hydroxide into carbonate. The solution, after filtering, was distilled under diminished pressure, a slow current of air being allowed to flow through the liquid during the distillation. After about one-third of the liquid had distilled over, the remainder was filtered to remove the barium carbonate which had been formed from the acid barium carbonate in solution by boiling. The remainder of the solution was then distilled under diminished pressure, using a new distilling flask so as to avoid the presence of a scratched surface.

We found that during this process the loss of hydrogen dioxide by decomposition was very great. The acid barium carbonate is not all decomposed by boiling in the earlier stages of the distillation, but gradually separates out as the distillation proceeds. The decomposition of the dioxide, which takes place very rapidly in the later stages of the distillation, is probably caused by the solid barium carbonate which has separated, or by the acid carbonate still remaining in the solution. On account of the great loss of material we abandoned the above method in favor of the following, which we found to be far more satisfactory.

The commercial hydrogen dioxide was treated with zinc oxide and allowed to remain in contact with the oxide over night. By this means any hydrochloric or other volatile acid present was converted into the zinc salt. The solution was then filtered to remove the excess of zinc oxide, and distilled on a water-bath under a pressure of from 60 to 90 mm. of mercury. The distillation was allowed to proceed slowly, the temperature being kept as low as possible. The first third of the distillate was discarded since it contained comparatively little dioxide. The distillation was continued until only a few cubic centimeters remained in the flask. The last two-thirds of the distillate contained the material used in this work.

The advantage of this method over the one in which barium

hydroxide was employed, is probably to be found in the fact that the zinc chloride formed is so very soluble that it does not separate from the solution during the distillation until nearly all of the liquid has been distilled off. If an attempt is made to distil the last few drops out of the flask, a vigorous decomposition of the dioxide sets in, probably due to the separation from this concentrated solution of some solid material.

The aqueous solution of hydrogen dioxide thus purified was concentrated by placing it in a new and unscratched evaporating dish, which was very gently warmed on a water-bath. The temperature of the solution of hydrogen dioxide should not be allowed to rise above 50°, and it is better if the evaporation of water from the solution took place at a lower temperature, especially after the concentration of the solution has become considerable. We at first attempted to concentrate the solution of hydrogen dioxide by allowing its temperature to rise to 70° or 75°, as Wolfenstein[1] had done, taking the precaution recommended by him of allowing only a small part of the evaporating dish to come in contact with the water-bath. At these elevated temperatures the loss in hydrogen dioxide by decomposition was so great that much lower temperatures were employed.

An Attempt to Apply the Conductivity Method.

Having obtained pure hydrogen dioxide by the above method, in any quantity desired, we tried to determine the conductivity of solutions of salts in aqueous hydrogen dioxide. It was obvious at the outset that the ordinary platinum plates could not be used for electrodes, since the dioxide would be decomposed by them. We had our platinum electrodes very highly polished by a silversmith, and we worked at zero degrees. But even at this low temperature the dioxide was sufficiently decomposed by the metal to cover the plates with oxygen before a reading could be made. The aqueous solution of dioxide used contained only from 6 to 10 per cent, yet, even at such dilutions, the decomposition was sufficient to prevent us from measuring the conductivity of the solutions.

[1] Ber. d. chem. Ges., **28**, 3309.

We then tried a large number of other metals to see if one could be found which would not decompose the dioxide. All of the metals tried decomposed the hydrogen dioxide to such an extent that they could not be used for electrodes. We were therefore compelled to abandon the conductivity method (for the present) as a means of measuring the dissociation of electrolytes in aqueous hydrogen dioxide.

The only method at our disposal was that based upon the lowering of the freezing-point of solvents by dissolved substances.

Application of the Freezing-Point Method.

It seemed probable that by comparing the lowering of the freezing-point of aqueous hydrogen dioxide with the lowering of the freezing-point of water produced by the same substances, we could form some idea as to the relative dissociating power of water and of hydrogen dioxide. The lowering of the freezing-point of water produced by solutions of potassium chloride, potassium carbonate, and sodium carbonate of various dilutions, was studied in the usual manner. The solutions were prepared from pure, recrystallized salts, by dissolving weighed quantities in water, in calibrated measuring flasks. In every case the normal solution was prepared by weighing the salt, dissolving it and diluting to a known volume. The more dilute solutions were made from the normal solution by diluting measured volumes in measuring flasks.

The solutions in aqueous hydrogen dioxide were prepared in exactly the same manner. The normal solutions were made by dissolving weighed quantities of the salts in the dioxide, in a measuring flask, and diluting with the dioxide to the required volume. During the solution of the salt both the salt and solvent were kept at zero degrees by surrounding the flask with ice, in order that there might be no appreciable decomposition of the dioxide. The more dilute solutions were prepared from the normal solution by adding a measured volume of the latter to a 50 cc. measuring flask and diluting to volume with the solution of the dioxide. The solu-

tion of salt and the dioxide were, in all cases, kept at zero degrees.

We at first convinced ourselves that the lowering of the freezing-point of water by the dioxide was normal, *i. e.*, a gram-molecular normal solution of the dioxide froze 1°.86 lower than pure water. This is the same as to say that the molecular weight of hydrogen dioxide in water, as determined by the freezing-point method, corresponds to the formula H_2O_2. In determining the freezing-point of the aqueous hydrogen dioxide, the concentration of the dioxide is changed by the separation of ice. This was taken into account and the correction applied in the usual manner, by observing the amount which the solution was undercooled. In a similar manner the correction for change in concentration was applied when the freezing-point of the solution of salt was determined.

The following results were obtained for three salts in water, and in aqueous hydrogen dioxide of two concentrations.

Potassium Chloride in Water.

Concentration. Gram-molecules per liter.	Observed lowering of freezing-point.	Molecular lowering of freezing-point.
1.0	3°.416	3.416
0.75	2°.517	3.356
0.50	1°.684	3.368
0.25	0°.860	3.440

Second Series.

1.00	3°.411	3.411
0.75	2°.540	3.388
0.50	1°.700	3.400

Only two concentrations of potassium chloride in hydrogen dioxide were studied. The solvent contained 4.6 per cent of the dioxide. The following results were obtained:

Potassium Chloride in Aqueous Hydrogen Dioxide (4.6 Per Cent).

Concentration. Gram-molecules per liter.	Observed lowering of freezing-point.	Molecular lowering of freezing-point.
1.0	3°.045	3.045
1.0	2°.995	2.995
0.5	1°.468	2.936
0.5	1°.460	2.920

These results show that the molecular depression of potassium chloride in aqueous hydrogen dioxide is much less than in water.

The following results were obtained with sodium nitrate :

Sodium Nitrate in Water.

Concentration. Gram-molecules per liter.	Observed lowering of freezing-point.	Molecular lowering of freezing-point.
1.0	$3^{\circ}.150$	3.150
0.5	$1^{\circ}.621$	3.242
0.25	$0^{\circ}.839$	3.356

Sodium Nitrate in Aqueous Hydrogen Dioxide (4.6 Per Cent).

Concentration. Gram-molecules per liter.	Observed lowering of freezing-point.	Molecular lowering of freezing-point.
1.0	$3^{\circ}.092$	3.092
1.0	$3^{\circ}.095$	3.095
0.5	$1^{\circ}.590$	3.180
0.25	$0^{\circ}.808$	3.232

Second Series.

1.0	$3^{\circ\cdot}109$	3.109
1.0	$3^{\circ}.110$	3.110
0.5	$1^{\circ}.596$	3.192

In the second series of experiments the solutions were prepared from entirely new material.

Sodium Nitrate in Stronger Hydrogen Dioxide (7 Per Cent).

Concentration. Gram-molecules per liter.	Observed lowering of freezing-point.	Molecular lowering of freezing-point.
1.0	$3^{?}.042$	3.042
0.5	$1^{\circ}.565$	3.130
0.5	$1^{\circ}.571$	3.142
0.25	$0^{\circ}.794$	3.176

The results obtained with sodium nitrate in aqueous hydrogen dioxide, like those obtained with potassium chloride, are smaller than the corresponding results in water as the solvent. To test still further the effect of the hydrogen dioxide on the freezing-point lowering, a more concentrated solution of hydrogen dioxide in water was used. The lowerings obtained in the latter case were still smaller than when the more

dilute hydrogen dioxide was employed. We would have used solutions of hydrogen dioxide of greater concentration, but the freezing-point of such solutions would be so low that some refrigerating agent other than salt and ice would have to be employed ; and it is difficult to regulate the temperatures of such very cold mixtures.

The results with potassium nitrate are even more striking than those with sodium nitrate. The freezing-point lowering of this salt in water, and in two solutions of hydrogen dioxide, was measured.

Potassium Nitrate in Water.

Concentration. Gram-molecules per liter.	Observed lowering of freezing-point.	Molecular lowering of freezing-point.
1.0	2°.656	2.656
0.75	2°.107	2.809
0.50	1°.470	2.940
0.25	0°.771	3.084

Potassium Nitrate in Aqueous Hydrogen Dioxide (5.3 Per Cent).

Concentration. Gram-molecules per liter.	Observed lowering of freezing-point.	Molecular lowering of freezing-point.
1.00	2°.164	2.164
0.75	1°.667	2.223
0.50	1°.190	2.380
0.25	0°.627	2.508

Potassium Nitrate in Stronger Hydrogen Dioxide (7 Per Cent).

Concentration. Gram-molecules per liter.	Observed lowering of freezing-point.	Molecular lowering of freezing-point.
1.00	1°.954	1.954
0.50	1°.057	2.114
0.25	0°.570	2.280

The lowering of the freezing-point of water by potassium nitrate is very much greater than the lowering of the freezing-point of aqueous hydrogen dioxide. The lowering becomes smaller, as we would expect, when the quantity of dioxide present is increased.

In all of these experiments the amount of the hydrogen dioxide present was determined after the salt had been intro-

duced, to see whether any appreciable decomposition of the dioxide had been effected by the salt. In no case was any appreciable change in the concentration of the dioxide detected.

The effect of the presence of hydrogen dioxide in water is, then, to diminish the lowering of the freezing-point produced by a dissolved salt. The question which naturally arises is, why is this the case ? The simplest explanation seems to be that the hydrogen dioxide either decreases the dissociation which has been effected by the water, or acts as a polymerizing agent upon the undissociated molecules present in the solution.

In the case of potassium nitrate it is difficult to see how the results obtained can be accounted for on the basis of polymerization. Indeed, the decrease in the molecular lowering, produced by the presence of the hydrogen dioxide, is so great in this case that we would suspect some combination had taken place between the potassium nitrate and the hydrogen dioxide. This point we propose to investigate.

This is but a preliminary investigation. Further work on the lowering of the freezing-point of aqueous hydrogen dioxide will be done in this laboratory.

CHEMICAL LABORATORY,
    JOHNS HOPKINS UNIV.,
        February, 1901.

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Several months after the above paper was written an account of an investigation on " Hydrogen Dioxide as an Acid," was presented to the German Electrochemical Society, by Bredig.[1] This has been recently described more fully by Calvert.[2]

Two facts brought out in this investigation are of special interest in this connection. It is shown that electrodes of iron covered with tin do not decompose dilute, alkaline, hydrogen dioxide, and can be used to measure the conductivity of such solutions. We shall try such electrodes in an extension of the above line of work.

[1] Ztschr. Elektrochem., **7**, 622.
[2] Ztschr. phys. Chem., **38**, 513.

It has also been shown by Calvert that a number of strong alkalies can combine with hydrogen dioxide, forming definite compounds with it. This renders it not impossible that our suggestion that potassium nitrate may have combined with some of the hydrogen dioxide, is the true explanation of the results which we obtained. It at least makes it highly desirable that this point should be tested by direct experiment.

JOHNS HOPKINS UNIV.,
December, 1901.

A STUDY OF TRIBROMPHENOLBROMIDE.

BY J. H. KASTLE.

The compound called tribromphenolbromide was discovered by Benedikt in 1879.[1] He obtained it in the form of beautiful yellow crystals, which were found to melt at 118° C. On heating it to 125° C. it was found to decompose, evolving one atom of bromine, and giving an amorphous derivative which Benedikt called hexabromphenoquinone. Benedikt made the further interesting observation that on heating the compound under sulphuric acid it underwent a molecular rearrangement whereby it was transformed completely and quantitatively into tetrabromphenol. Benedikt further investigated the action of tribromphenolbromide on alcohol, tin and hydrochloric acid, aniline and phenol. In every case he obtained ordinary tribromphenol as a final product. He was therefore led to assign to the compound the following structural formula as that best comporting with the general behavior of the substance ; *viz* :

$$C_6H_2Br_3(OBr).$$
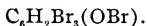
In other words, he looked upon tribromphenolbromide as a derivative of tribromphenol in which the hydroxyl hydrogen of the latter had been replaced by bromine.

It seemed to the writer therefore to offer a fruitful field for further investigation, especially as the constitution of the compound, as determined by Benedikt, seemed to rest upon very

[1] Ann. Chem. (Liebig), **199**, 127.

slender lines of evidence, and inasmuch further as no satis-
factory explanation was offered for the remarkable molecular
rearrangement which the compound undergoes under sul-
phuric acid. This investigation was begun in 1899. Unfor-
tunately, it has been interrupted at various times by other
work of a more pressing character, and is even yet incom-
plete. It is believed, however, that certain results already
reached are of sufficient interest to warrant publication in
their present form. The work has been done in collaboration
with certain of the advanced students of the chemical depart-
ment here, *viz.*, A. S. Loevenhart, Rosa Speyer, and J. W.
Gilbert.

PREPARATION AND PROPERTIES OF TRIBROMPHENOLBRO-
MIDE. CONDUCT OF TRIBROMPHENOLBROMIDE TOWARDS
HEAT AND LIGHT. ACTION OF TRIBROMPHENOL-
BROMIDE ON WATER, POTASSIUM IODIDE, AND
ZINC ETHYL. BEHAVIOR OF TRIBROM-
PHENOLBROMIDE TOWARDS BROMINE
AND IODINE.

BY A. S. LOEVENHART.

Tribromphenolbromide was prepared essentially according
to Benedikt's method by adding an aqueous solution of phe-
nol to one of bromine containing the bromine slightly in ex-
cess of the amount required. Usually a solution containing
4.7 grams of phenol was added to bromine water containing
13 cc. of bromine, and the mixture thoroughly shaken and
allowed to stand for several hours. Under these conditions
the tribromphenolbromide separates as a yellow granular pre-
cipitate, altogether different in appearance from tribrom-
phenol. It has been found best to filter the substance through
fine cotton cloth. After washing with water the compound
was transferred to filter-paper and allowed to dry in the air,
in the dark and at ordinary temperatures. Tribromphenol-
bromide is thus obtained in the form of a buff-colored powder.
On analysis it was found to contain 19 per cent of easily re-
placeable bromine. As observed by Benedikt, the compound

can be obtained in beautiful crystalline condition by crystallizing from hot chloroform. On cooling, it separates from its solution in chloroform in the form of beautiful lemon-yellow plates or prisms melting at 118° C. Up to a certain limit the crystals become lighter in color the oftener the compound is recrystallized from chloroform. For reasons, to be discussed in a subsequent part of the paper, the compound is best preserved in open vessels and not in tightly stoppered bottles. The molecular weight of the compound was determined by the freezing-point method, using ethylene bromide as the solvent. An average of three concordant determinations gave 412.5 as the molecular weight. The calculated molecular weight of the compound is 410.

Conduct of Tribromphenolbromide Towards Heat and Light.

According to Benedikt, when tribromphenolbromide is heated it melts at 118° C. to a reddish liquid. If the temperature be raised to 125° C. the compound begins to decompose, evolving free bromine. If the compound be heated for some time at 130° C. in a current of carbon dioxide it loses 1 atom of bromine for each molecule of the compound decomposed, and there is left behind a reddish substance having much the appearance of molten sulphur. On dissolving this gummy mass in ether and adding alcohol to the solution a white amorphous substance is obtained, which, according to Benedikt, is hexabromphenoquinone,

$$C_6H_2Br_3O—OBr_3H_2C_6.$$
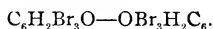
In the hope of throwing some further light on the constitution of this substance, and thereby learning something more of the nature of tribromphenolbromide itself, the attempt was made to synthesize hexabromphenoquinone from tribromphenolbromide and silver tribromphenolate in the following manner: Ten grams of finely powdered tribromphenolbromide were placed in a flask together with 30 cc. af chloroform and 10.5366 grams of silver tribromphenolate were added gradually. The reaction took place at once at ordinary temperatures, and after shaking thoroughly and standing for some time it was filtered from the silver bromide. The resi-

due was found to consist entirely of silver bromide. On the addition of alcohol to the filtrate it was found to yield a white flocculent precipitate, which proved to be identical in every respect with Benedikt's hexabromphenoquinone.

On the Action of Sunlight on Tribromphenolbromide in Solution in Carbon Bisulphide.

As already stated in the above, tribromphenolbromide in pure condition has, in the solid state, a beautiful yellow color. When dissolved in carbon bisulphide it imparts a yellow color to the solution, and if kept in the dark such solutions retain their yellow color unaltered for almost any length of time. Such solutions, however, have been found to change slowly, even in diffused light, and in the direct sunlight they rapidly assume the characteristic color of free bromine in solution in carbon bisulphide. Such having been found to be the case, it was decided to follow the decomposition in direct sunlight colorimetrically by comparing the solutions of tribromphenolbromide which had been exposed to the light for a given time with freshly prepared solutions of bromine in carbon bisulphide of known strength. A N/10 solution of tribromphenolbromide was made up in the dark and then exposed to direct sunlight, portions being removed from the flask from time to time for comparison with the standard solution of free bromine. The color comparisons were made in small Nessler cylinders of 30 cc. capacity and all having the same internal diameter. When the solution of tribromphenolbromide had become too deeply colored to make accurate comparisons possible, aliquot portions were removed from the flask and diluted to a given volume so as to get more accurate results. The color comparisons were always made on volumes of 10 cc. The following are the results obtained :

Time in minutes.	Percentage decomposition calculated for 1 atom of bromine.
32	67.90
45	84.87
57	113.25
67	141.51
84	181.20
99	181.20
140	201.60

From these colorimetric measurements it became evident that in the sunlight 2 atoms of bromine are liberated from each molecule of tribromphenolbromide, or that there is some other highly colored substance produced. In order to prove absolutely that it was free bromine which imparted the yellow color to the solution, 250 cc. of a N/10 solution of tribromphenolbromide in carbon bisulphide was prepared. This was exposed to the direct sunlight for six days. At the end of this time 10 cc. of the solution were removed from the flask and an excess of an aqueous solution of potassium iodide added. This was then titrated with decinormal thiosulphate. It required 16.45 cc. As the original solution fumed strongly in the air it was thought advisable to determine the total bromine by reducing with zinc dust and titrating with N/10 silver nitrate and ammonium sulphocyanate. It was found that each cubic centimeter of the solution contained 0.01468 gram of bromine in the form of free bromine and hydrobromic acid. Some of the original solution was now distilled at the lowest possible temperature. It was found that the distillate contained 0.01316 gram of free bromine and 0.00076 gram of bromine as hydrobromic acid per cubic centimeter. An equal amount of the bromine which went to form hydrobromic acid must have disappeared in the substitution. We have thus accounted for 0.01468 gram of bromine out of the 0.016 gram of bromine per cubic centimeter which should have been present in the solution if each molecule of tribromphenolbromine had liberated 2 atoms of bromine. The gummy mass left behind in the flask, after the distillation, was dissolved in chloroform and precipitated by the addition of alcohol. After several such precipitations it was obtained as a white, amorphous precipitate. A bromine determination was made on this compound with the following result :

	Calculated for $(C_6H_2Br_2O)_2$.	Found.
Br	64.00	64.46

In its physical properties this compound was found to be very similar to hexabromphenoquinone described in the above. Up to this time it has not been found possible to obtain it in

crystalline condition, and hence its constitution has not yet been settled definitely.

The Action of Water on Tribromphenolbromide.

In view of the ease with which tribromphenolbromide decomposes, both when heated in the solid state and in solution in organic solvents, it occurred to us that it might prove of interest to try its conduct towards water at high temperature. Accordingly, 5 grams of tribromphenolbromide were heated in a hard glass tube with 5 cc. of water, for ten hours, at 100° C. After a few minutes' heating on the water-bath the tube was observed to contain some bromine vapor, which, however, shortly disappeared. At the conclusion of the experiment the substance in the tube was found to be in a molten condition, but solidified on cooling. On opening the tube it was found that no pressure had developed. The supernatant liquid contained only a trace of bromine but was found to contain large quantities of hydrobromic acid. The solid mass was found to consist of a mixture of tribromphenol and tetrabromquinone. Hence the reaction must, in all probability, have taken place according to this equation :

$$3C_6H_2Br_2(OBr) + 2H_2O = \\ 2C_6H_2Br_3(OH) + C_6Br_4O_2 + 2HBr + H_2O.$$
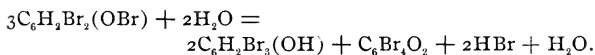
Action of Potassium Iodide on Tribromphenolbromide.

Tribromphenolbromide was found to be capable of setting free iodine from solutions of potassium iodide. It occurred to us, in this connection, that it might be possible to prepare tribromphenoliodide by means of this reaction. In order to test this point, 8 grams of tribromphenolbromide were ground to a fine powder and mixed with a slight excess of potassium iodide. The mass turned brown in color at once, indicating that the reaction between these two substances had begun even in the solid state. Before the reaction had proceeded far, however, 30 cc. of chloroform were added and the flask sealed and allowed to stand several days. On opening the flask it was found that the solution contained a large amount of free iodine, thereby indicating that the reaction had not oc-

curred in the manner hoped for. On adding alcohol to some of the solution obtained in the above, a precipitate of hexabromphenoquinone was obtained. The reaction of potassium iodide on tribromphenolbromide is therefore, in all probability, to be represented by the following equation :

$$2C_6H_2Br_3(OBr) + KI = C_6H_2Br_3O—OBr_3H_2C_6 + KBr + BrI.$$
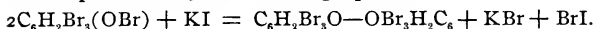
It should be observed, however, that this reaction proceeds in this manner only in the absence of water, as may be seen from the following experiment : 0.205 gram of tribromphenolbromide were dissolved in 10 cc. of carbon bisulphide, and 25 cc. of water were added and an excess of potassium iodide. The free iodine was titrated with $N/10$ thiosulphate solution. The amount of thiosulphate solution required was found to vary between 9 and 10 cc., according to the relative amounts of water, carbon bisulphide, and potassium iodide present. Further, the supernatant aqueous solution gave, when acidified, a copious precipitate of tribromphenol. In aqueous solution, therefore, the action of potassium iodide on tribromphenolbromide takes place according to the following equations :

$$2C_6H_2Br_3(OBr) + 2KI = 2C_6H_2Br_3OK + Br_2 + I_2,$$
and $Br_2 + 2KI = 2KBr + I_2$.
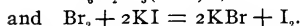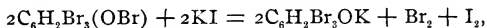
This would account for the double amount of iodine set free. We see thus that tribromphenolbromide decomposes potassium iodide by virtue of the easily replaceable bromine which it contains, and also for the reason that it is an oxidizing agent. It will be observed, further, that in solution in organic solvents tribromphenolbromide tends toward the production of hexabromphenoquinone, whereas in aqueous solutions it tends towards the production of tribromphenol.

Action of Zinc Ethyl on Tribromphenolbromide.

If the constitution of tribromphenolbromide is correctly represented by Benedikt's formula, $C_6H_2Br_3(OBr)$, one would naturally expect to obtain ethyl tribromphenolate,

$$C_6H_2Br_3(OC_2H_5),$$
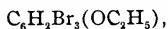
by treating it with zinc ethyl. In order to test this point,

equivalent quantities of tribromphenolbromide and zinc ethyl were brought together in absolute ether. A vigorous reaction occurred, but instead of obtaining ethyl tribromphenolate and zinc bromide, we obtained ethyl bromide and the zinc salt salt of tribromphenol. In other words, the reaction between these two substances occurs in a manner exactly the reverse of what one would naturally expect if Benedikt's view of the constitution of the compound is correct. The significance of this result will be discussed in a subsequent part of the paper.

Action of Iodine on Tribromphenolbromide.

In the hope of being able to prepare tribromphenoliodide it occurred to us to try the action of iodine on tribromphenolbromide. With this in view, 5 grams of tribromphenolbromide were dissolved in carbon bisulphide, and to this solution the calculated amount of iodine, 1.5 grams, was added and the solution well shaken. It soon became evident that some reaction had taken place, for the carbon bisulphide solution soon lost its violet color and assumed a brownish tint instead. After standing about two and a half hours the solution was distilled at the lowest possible temperature, the distillate showing the same brownish color as the solution itself. The distillate was tested both for bromine and iodine with the result that both were found to be present. The residue left in the distilling bulb was dissolved in chloroform and the solution precipitated with alcohol. The amorphous white precipitate thus obtained was shown to be hexabromphenoquinone. The action of iodine on tribromphenolbromide can therefore be represented by the following equation :

$$2C_6H_2Br_3(OBr) + I_2 = C_6H_2Br_3O\text{---}OBr_3H_2C_6 + 2BrI.$$
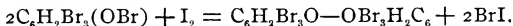
The Catalysis of Tribromphenolbromide by Bromine Vapor.

It was observed that tribromphenolbromide could not be preserved as well in tightly stoppered bottles as by freely exposing it to the air. This seemed to indicate that the traces of free bromine resulting from the slight decomposition of the compound at ordinary temperatures, if not removed, acted by

catalysis to greatly accelerate the decomposition of the rest of the compound. In order to test this point the following experiments were tried : Four tubes were prepared, each containing 0.5 gram of pure tribromphenolbromide. Into two of these, small amounts of bromine vapor were introduced. These tubes, together with the two containing no bromine, were then sealed. Two of the tubes, one containing bromine vapor and the other without, were kept in the dark for four days. A similar pair of tubes was exposed to the direct sunlight for eight hours. On examining the tubes that had been exposed to the direct sunlight, the next day, it could be easily seen that the greatest decomposition had occurred in the tubes containing the bromine vapor. The tubes were then opened and the vapor of bromine removed by a current of air. The material in the tubes was then carefully washed out with chloroform and an excess of an aqueous solution of potassium iodide added, and the free iodine titrated against $N/10$ thiosulphate solution. If none of the compound had decomposed, it would have required 24.4 cc. of thiosulphate. As a matter of fact, the tube containing the tribromphenolbromide without bromine required 22.65 cc. of the thiosulphate, corresponding to a decomposition of 7.13 per cent, while the tube containing the bromine vapor required only 17.65 cc., corresponding to a decomposition of 27.63 per cent. In other words, by means of a trace of bromine the decomposition of tribromphenolbromide had been accelerated nearly fourfold. The second pair of tubes was allowed to remain in the dark four days, when they were opened and the bromine vapor removed by a current of air. The residues were titrated with sodium thiosulphate after the addition of potassium iodide. The tube which did not contain bromine vapor originally, required 23.47 cc. of thiosulphate, corresponding to a decomposition of 3.77 per cent, while the tube containing the bromine vapor originally, required 16.95 cc. of thiosulphate, corresponding to a decomposition of 30.5 per cent. In this case the decomposition of tribromphenolbromide had taken place eight times faster in the presence of bromine than without. The great acceleration of the decomposition of this compound

by a small amount of bromine vapor is a very remarkable and noteworthy fact.

THE CONSTITUTION OF TRIBROMPHENOLBROMIDE. THE PREPARATION AND PROPERTIES OF TRIBROMPHENYL-SULPHONATE. THE CONVERSION OF TRIBROM-PHENOLBROMIDE INTO METADIBROM-QUINONE.

BY ROSA SPEYER.

After some time the investigation of tribromphenolbromide was resumed at this point, for the reason that the constitution of the compound could not yet be looked upon as definitely settled either in favor of or against Benedikt's view. The peculiar conduct of the compound towards zinc ethyl, as pointed out in the preceding paper, still left the matter in doubt, although the formation of zinc salt of tribromphenol rather than its ethyl ether would seem to indicate that Benedikt's formula is incorrect, and that tribromphenolbromide is by no means as simple as he represented it to be. In order to throw further light upon this subject, it occurred to us that it might be well to attempt the preparation of the tribromphenyl ether of benzenesulphonic acid by two distinct methods, the first being by the action of benzenesulphonchloride on sodium tribromphenolate ; the second being by the action of sodium benzenesulphinate on tribromphenolbromide. Should both of these reactions yield the same sulphonic ether, it would probably be regarded as tolerably certain proof of the correctness of Benedikt's formula for this compound.

Tribromphenyl Benzenesulphonate,
$$C_6H_5SO_2.OC_6H_2Br_3.$$
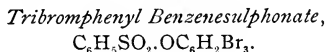
This ether is readily prepared by the action of sodium tribromphenolate on benzenesulphonchloride. The sulphonchloride is dissolved in absolute ether, and to this solution finely powdered anhydrous sodium tribromphenolate was added, in small quantities at a time and with constant shaking, until a considerable excess had been added. The solution was then filtered and the clear filtrate allowed to evap-

orate spontaneously at ordinary temperature, when the sulphonic ether was obtained. A still better method 'for the preparation of the ether is the following : The sodium salt of tribromphenol is dissolved in absolute alcohol, and to this solution there is added the theoretical quantity of benzenesulphonchloride and the solution heated to boiling. On filtering from the sodium chloride and cooling, the sulphonic ether crystallizes out. It may be purified by dissolving in alcohol and treating with animal charcoal. The ether crystallizes from alcohol in the form of colorless, glistening, rhombic plates. It melts at 99° C. (uncorr.) It is insoluble in water and cold alcohol. It is readily soluble, however, in hot alcohol, benzene, carbon bisulphide, acetone, and ethyl ether. From hot concentrated solutions in alcohol it frequently separates as an oil which solidifies, on cooling, to a white crystalline mass. The nature of the compound thus obtained was was determined by saponification with alcoholic caustic soda. To saponify 0.2353 gram of the ether, 5 cc. of N/10 caustic soda were required. Theory for $C_6H_5SO_2.OC_6H_2Br_3$, 5 cc. N/10 NaOH.

Unlike most of the sulphonic ethers, known to us at present, this compound has been found to be remarkably stable towards water and other hydrolyzing agents.

Action of Sodium Benzenesulphinate on Tribromphenolbromide.

In order to determine whether tribromphenyl benzenesulphonate could be formed from tribromphenolbromide, a quantity of benzenesulphinic acid was prepared by Gattermann's method and converted into the sodium salt. A small quantity of tribromphenolbromide was then dissolved in carbon bisulphide, and to this solution the theoretical amount of finely powdered sodium benzenesulphinate was added, and the mixture thoroughly shaken. After standing for an hour the solution was filtered. The white residue was found to consist of sodium bromide. On allowing the filtrate to evaporate spontaneously, a reddish gummy substance was obtained, together with a smaller quantity of an oily product having the characteristic odor of a sulphonchloride or bromide. The

gummy substance was identified as Benedikt's hexabromphenoquinone. Hence the reaction between the sodium benzenesulphinate and tribromphenolbromide does not result in the formation of a sulphonic ether but takes place in the sense of this equation :

$$2C_6H_2Br_4O + C_6H_5SO_2Na =$$
$$(C_6H_2Br_3O)_2 + NaBr + C_6H_5SO_2Br.$$

Action of Silver Nitrate on Tribromphenolbromide.

Beyond proving the incorrectness of Benedikt's formula for tribromphenolbromide, but little tangible evidence of the real nature of the compound has been obtained up to this time. It occurred to us in this connection, however, to test the conduct of silver nitrate towards tribromphenolbromide. On boiling a solution of silver nitrate, to which some tribromphenolbromide had been added, it was observed that a crystalline precipitate was thrown down. This was filtered off and purified by dissolving in alcohol and reprecipitating with water, when the substance was obtained in the form of yellow iridescent laminae. The compound was still further purified by sublimation. It was observed to melt at 131° C. The compound was identified as metadibromquinone by comparing it with some of this compound prepared by the method of Levy and Schultz.[1] About the time this observation was made, Thiele and Eichwede[2] also obtained metadibromquinone from tribromphenolbromide by treating the latter substance in acetic acid solution with lead acetate. These observers came to the conclusion, therefore, that tribromphenolbromide has a quinone structure, and that its chemical behavior can best be interpreted by the following graphic formula :
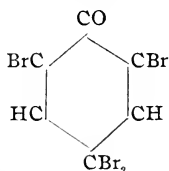
[1] Ann. Chem. (Liebig), **210**, 159.
[2] Ber. d. chem. Ges., **33**, 673 (1900).

In view of the simple relation existing between tribromphenolbromide and metadibromquinone, it would seem possible to pass from the one of these substances to the other by a number of simple reagents, such as silver oxide, calcium carbonate, etc. This, however, has not been our experience, possibly for the reason that the proper solvent was not employed. Of all the reagents thus far tried, fuming nitric acid has been found to give the largest yield of metadibromquinone from tribromphenolbromide.

ON THE MOLECULAR REARRANGEMENT OF TRIBROMPHENOLBROMIDE BY MEANS OF SULPHURIC ACID.

BY J. W. GILBERT.

As already stated above, the most interesting property of tribromphenolbromide is that when heated to 118° C., under sulphuric acid, it undergoes a molecular rearrangement whereby it is transformed completely into tetrabromphenol. This remarkable molecular rearrangement was first described by Benedikt, who pictured the change as occurring in this manner :

$$C_6H|H|Br_3O|Br| \atop |Br|OBr_3|H|HC_6 = 2C_6HBr_4OH.$$
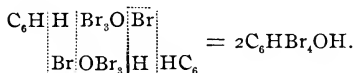
Obviously this explanation is by means satisfactory, since it entirely ignores the part played by the sulphuric acid, and since, further, the rearrangement in question cannot be brought about by heat alone. A further study of this molecular rearrangement was therefore undertaken in the hope of being able to determine the part played by the sulphuric acid in the change. On heating tribromphenolbromide under sulphuric acid, as directed by Benedikt, it was observed that the substance melted under the sulphuric acid at 113° C. It was thought from this, therefore, that possibly the sulphuric acid could bring about the change in question without the aid of heat.

With the view of testing this point some finely powdered

tribromphenolbromide was mixed with concentrated sulphuric acid at ordinary temperature. It was observed that the compound underwent a change of color and gradually became perfectly white. The acid was then poured off and the compound washed with water and purified by crystallizing from alcohol to which an equal volume of boiling water had been added. The substance was finally obtained in the form of white, felt-like needles, which were found to melt at 109° C. This compound is tetrabromphenol, and the fact that it is formed under these circumstances certainly goes to show that the molecular rearrangement of tribromphenolbromide is due to the sulphuric acid and not to an elevation of temperature. In order to determine whether the molecular rearrangement could be brought about by other substances, the conduct of tribromphenolbromide was tried towards the following reagents : Paraffine, dibrombenzene, glycerine, concentrated hydrochloric acid, glacial acetic acid, dilute sulphuric acid, benzenesulphonchloride, benzenesulphonic acid, a saturated solution of iodic acid, sodium acid sulphite, carbon tetrachloride, potassium bromide, and potassium chloride.

Nearly all of these substances were found to decompose tribromphenolbromide, especially at high temperatures, but in no case was the molecular rearrangement brought about.

That it is not due to acids in general may be seen from the following : A quantity of tribromphenolbromide was allowed to stand for one week under concentrated hydrobromic acid. At the end of this time the compound was found to have lost its color and to have become white. The substance was filtered from the hydrobromic acid, washed with water, and recrystallized. It was found to melt at 91° C. and was found to be identical in every respect with tribromphenol. That undissociated acids in general do not bring about the molecular rearrangement was proved by dissolving tribromphenolbromide in a concentrated solution of hydrochloric acid in chloroform. Some of this solution was heated in sealed tubes, after which the chloroform was allowed to evaporate off, when tribromphenolbromide was obtained in unaltered condition.

These results leave practically no room for doubt that the

molecular rearrangement of tribromphenolbromide is accomplished solely by the action of concentrated sulphuric acid.

Trichlorphenolbromide.

In this connection, however, it should be noted that it is stated in Watts' "Chemical Dictionary" and Beilstein's "Organische Chemie," that trichlorphenolbromide, an analogous compound, is transformed by heating under water into an isomer, probably trichlormonobromphenol. In view, therefore, of what had been observed concerning the molecular rearrangement of tribromphenolbromide it was thought advisable to repeat this experiment.

Accordingly, trichlorphenolbromide was prepared in the following manner: Trichlorphenol was converted into the sodium salt by treating with the required amount of caustic soda. Five grams of the sodium salt thus obtained were dissolved in 500 cc. of water. To this solution 3 cc. of concentrated hydrobromic acid were added. The pasty mass thus obtained was immediately poured into a saturated solution of bromine containg 5 cc. of bromine. The mixed solution was thoroughly shaken and allowed to stand for some time. Trichlorphenolbromide separated from this solution in the form of a light-yellow, granular precipitate, altogether similar in appearance to tribromphenolbromide. The compound was purified by crystallizing from hot chloroform. In pure condition it was found to melt at 97° C. Like tribromphenolbromide, this substance is lemon-yellow in color but more soluble in chloroform than the former. The amount of easily replaceable bromine in trichlorphenolbromide was determined by reducing it with sodium acid sulphite and titrating with N/10 silver nitrate. 0.2 gram of the compound was taken for analysis.

	Calculated for Trichlorphenolbromide.	Found.
Br	0.577	0.564

Some of this compound, when ground to a fine powder and melted under water, was found to decompose with evolution of bromine. It was not transformed, however, into the isomeric

trichlormonobromphenol. On the other hand, trichlorphenol-
bromide is readily transformed by sulphuric acid into trichlor-
monobromphenol. In order to show this, 0.5 gram of tri-
chlorphenolbromide was heated under sulphuric acid. On
cooling, the acid was poured off and the residue washed with
water. The residual acid and washings were tested for bro-
mine with silver nitrate with negative result. The trichlor-
monobromphenol formed in this experiment was found to
weigh, when air-dried, 0.508 gram. It will be observed,
therefore, that it is the sulphuric acid and not the water which
effects the conversion of trichlorphenolbromide into trichlor-
monobromphenol.

In view of these results, therefore, there can be no doubt
that the conversion of tribromphenolbromide into tetrabrom-
phenol is brought about by means of concentrated sulphuric
acid.

The question naturally presents itself, how can sulphuric
acid accomplish this change? In answer to this the follow-
ing explanation has suggested itself in the light of Thiele and
Eichwede's formula for tribromphenolbromide, which, in view
of the former's[1] ideas of partial valence, may be written as fol-
lows:

I.
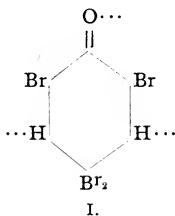
From what we know of the manner in which sulphuric acid
dissociates as an electrolyte, it would seem probable, at least,
that in its action on tribromphenolbromide the hydrogen ion
would add itself to the quinone oxygen of the compound,
thereby converting it into a phenol hydroxyl group. The

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[1] Thiele: Zur Kentniss der ungesättigten Verbindungen. Ann. Chem. (Liebig),
306, 129.

HSO_4 ion could then unite with either of the unsaturated groups in the meta position in the ring. This change may be represented graphically as follows :

II.
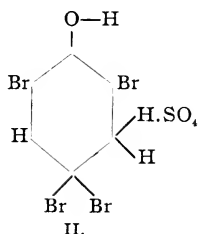
If now, from compound II, hydrobromic acid were to be split off, and there is every reason for supposing that such a decomposition might occur, there would remain a compound having the nature of an acid ester sulphate, thus :

III.
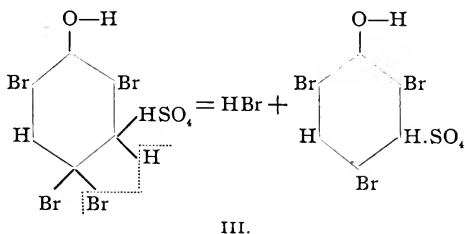
From what we know of the ease with which acid ethyl sulphate, $C_2H_5HSO_4$, is decomposed by hydrobromic acid to form ethyl bromide and sulphuric acid, it would seem logical to suppose that the hydrobromic acid resulting from the decomposition of compound II. would at once act upon compound III., with the production of tetrabromphenol and sulphuric acid, thus :

$$\text{III} \; (\text{O—H ring, Br, Br, H, HSO}_4 + \text{H Br, Br}) \; = \; H_2SO_4 + \text{IV} \; (\text{O—H ring, Br, Br, H, Br, Br})$$

III.   IV.
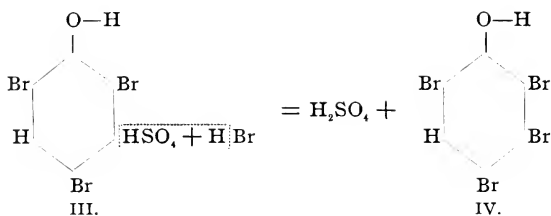
It will be observed that, like many other catalytic processes, the change in question is of a cyclical character. It is believed, further, that all changes brought about by electrolytes on tribromphenolbromide can be explained by the supposition that the hydrogen or positive ion enters into combination with the quinone oxygen of the compound, thereby converting it into a phenol or one of its salts. The negative ion probably enters into combination with one of the meta groups in the ring, and finally, as the result of cleavages occurring between the atoms or groups in the meta and para positions, the end products of the reaction are produced. For example, as shown in the above, tribromphenolbromide is reduced to tribromphenol by means of hydrobromic acid. It is believed that the changes taking place can be represented as follows:

$$(\text{O}\cdots \text{ ring, Br, Br, }\cdots\text{H, H}\cdots, \text{ Br, Br}) + HBr = (\text{O—H ring, Br, Br, H, H, Br, Br, Br}) =$$

$$(\text{O—H ring, Br, Br, H, H, Br}) + Br_2$$
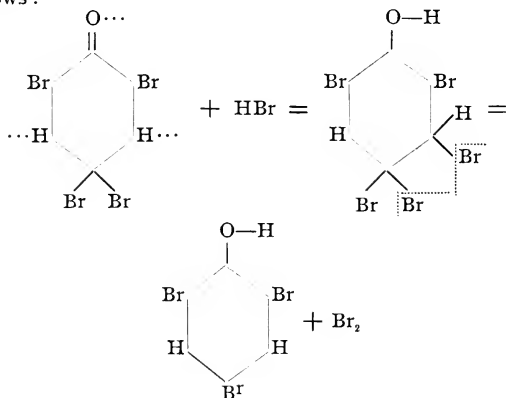
In the same way we can explain the action of potassium iodide on tribromphenolbromide, as may be seen from the following :
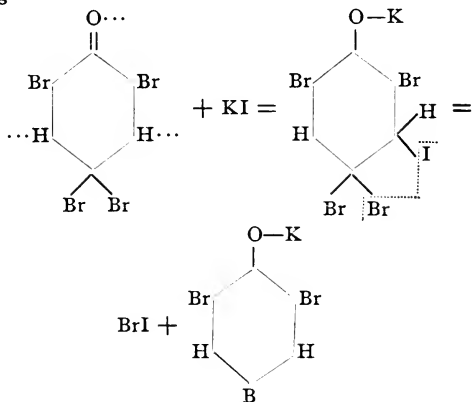
and, similarly, we can account for the action of zinc ethyl on this compound, thus :

4-27
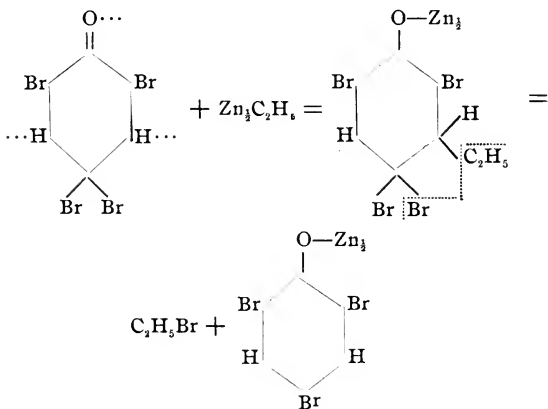
On the other hand, with electronegative elements such as bromine and iodine, which, as we have seen, also decompose tribromphenolbromide, and which have little or no affinity for the quinone oxygen, the case is somewhat different. Here the addition probably takes place on one of the groups in the meta position in the ring, with the production of an unstable intermediate product which, as the result of secondary changes occurring between the atoms or groups in the meta and para positions, gives the final products of the decomposition.[1] Thus, in the catalysis of tribromphenolbromide by means of bromine vapor, we probably have the following changes occurring:
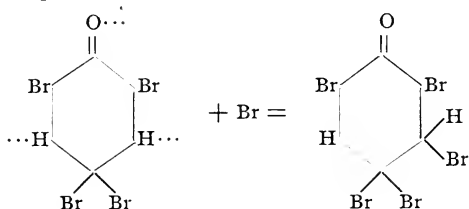
and
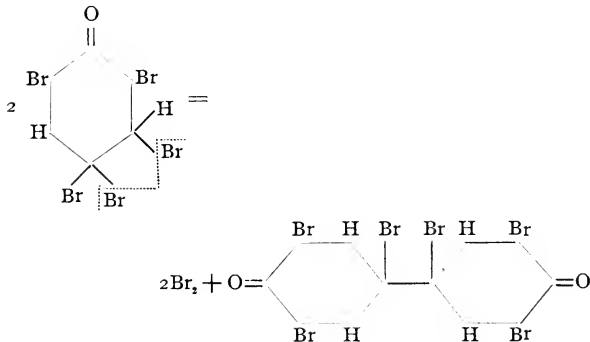
and, inasmuch as more and more bromine is produced the longer the reaction proceeds, we can readily understand how

[1] Thiele : Zur Kentniss der ungesättigten Verbindungen. Ann. Chem. (Liebig), **306**, 133.

a mere trace of bromine is all that is needed to start the decomposition. A similar explanation holds for the action of iodine upon tribromphenolbromide in solution. Finally, it should be observed that the quinone formula for tribromphenolbromide enables us to account satisfactorily for the decomposition of tribromphenolbromide by heat, whereby 1 atom of bromine is evolved from each molecule of the compound undergoing decomposition. The fact that two of the bromine atoms in this derivative are in combination with the same carbon atom indicates that in tribromphenolbromide we have to do with essentially the same sort of instability that is met with in the hexabrom addition-product of benzene itself, and it will be recalled that in this compound one of the atoms is readily lost from each carbon atom.

Further, if 1 atom of bromine is given up by the molecule of tribromphenolbromide, an unsaturated residue is left, two of which would in all probability unite to form Benedikt's hexabromphenoquinone. It follows further, from the above considerations, that the two quinone residues in hexabromphenoquinone are not united through the oxygen atoms, as was supposed by Benedikt, but rather through the para-carbon atoms. Thus the decomposition of tribromphenolbromide by heat may be represented as follows:
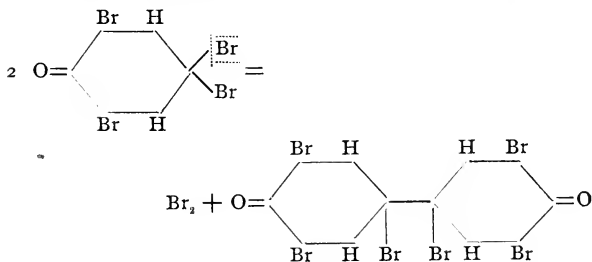
The formation of hexabromphenoquinone from tribromphenolbromide is certainly one of the most characteristic properties of the latter substance. On account of its amorphous character, however, and its great stability, but little is known of its chemical nature, and further work is necessary for a

clear understanding of this compound and its relation to tri-bromphenolbromide.

The loss of 2 atoms of bromine from the compound, which occurs on the exposure of a carbon bisulphide solution of tribromphenolbromide to light, is much more difficult to explain. Here also the product of the reaction is amorphous and exceedingly stable, and in fact shows many points of resemblance to hexabromphenoquinone. Like this compound, it probably contains two benzene residues, and tentatively, at least, we may represent its formation in the following manner:
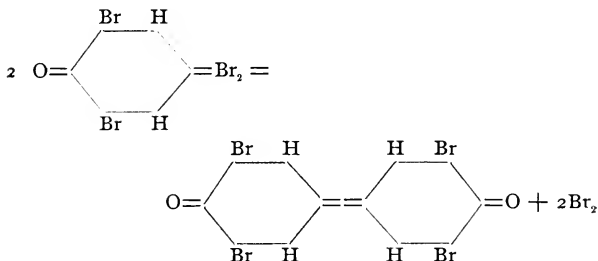
A further study of this compound is necessary, however, to a better understanding of the decomposition of tribromphenol-bromide by light.

State College of Kentucky,
Lexington, Ky., July, 1901.

SOLUBILITY OF MIXTURES OF SODIUM SULPHATE AND SODIUM CHLORIDE.[1]

By Atherton Seidell.

The solubility in water of mixtures of several pairs of electrolytes, in which one member of the pair is relatively much less soluble than the other, has lately been investigated in this laboratory by Dr. Frank K. Cameron and the author.[2] In connection with this work, the results presented in this paper were obtained, on mixtures of a pair of salts yielding a common ion, presumably, and having the additional feature that

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[1] Published by permission of the Secretary of Agriculture.

[2] Solution studies of salts occurring in alkali soils, Bulletin 18, Division of Soils, U. S. Department of Agriculture.

both members of the pair are readily soluble. A good deal of work of this description has been done in recent years, but so far as I am aware, this pair of salts has not previously commended itself to investigators, owing probably to the well-known tendency of sodium sulphate and its hydrates to form supersaturated solutions, which are difficult to handle ; and to the further fact, that salts which separate in the solid phase without water of crystallization, have hitherto appealed to investigators on account of the readiness with which the total amount of salt in solution may be determined by evaporation and drying, thus affording obvious analytical advantages in dealing with them.

In a few instances more than one investigator has worked with the same pair of salts, but a comparison of the results obtained was not possible, since the results were expressed in the one case in terms of grams of salts dissolved in a given weight of solvent, and in the other in terms of the grams of salts dissolved in a given volume of solution, and since the weights of the solutions were not given, there is no satisfactory way by which the results may be calculated to the same basis.

A recognition of the above fact is very important in all such work upon mutual solubility effects, and in order that the results may be of the greatest usefulness they should be presented in both ways.

EXPERIMENTAL WORK.

Before proceeding to a discussion of the results, a short description will be given of the manner in which the experimental work was carried on. In the majority of cases studied by other investigators, the salts with which they worked are such as crystallize without water of crystallization ; hence it was possible for these investigators to make determinations of the total grams of salts in solutions by evaporation, and then by a determination of one of the constituents to obtain the other by difference. In the case under consideration, however, it was found necessary to make the determination of each of the salts in the weighed portion of the solution. The sodium chloride was determined by calculating from the re-

sults of titrations with N/10 solution of silver nitrate ; and the sodium sulphate by calculating from the grams of barium sulphate, obtained by precipitation in the usual way.

The series of solutions were made up in bottles and so prepared that the amount of sodium sulphate should be in excess in the bottles with the lower numbers, the amount of sodium chloride gradually increasing from the second bottle on. In the bottles with the higher numbers the sodium chloride was in excess, and the amount of sodium sulphate gradually diminished. The first bottle contained only sodium sulphate in solution, the last only sodium chloride. Care was exercised in the determinations made at the several temperatures to have more than one bottle containing both salts present as solid phases in order that the point of intersection of the two curves representing the solubility of each salt in solutions of the other should be accurately determined. The bottles thus prepared and stoppered tightly were placed in a constant-temperature water-bath, in which they were rotated in a manner causing thorough agitation of the solutions for periods of eighteen to twenty-four hours. After the period of agitation the bottles were allowed to remain upright in the bath long enough for the solid material to subside and leave the supernatant solution clear. A 50 cc. portion of each solution was withdrawn by means of a pipette and transferred to a weighing-bottle and the weight of the solution taken. This amount of solution was then washed into a larger graduated flask, and, after diluting sufficiently, aliquot portions were taken for analysis as already described.

The results of the analyses at the various temperatures are given in the accompanying tables. In each case the weights of a given volume of the solutions are given in the first column. The grams of NaCl and Na_2SO_4 present in this volume are given in the second and third columns. The grams of sodium chloride and sodium sulphate present in 100 grams of water are given in the fourth and fifth columns, and finally the gram-molecules of sodium chloride and sodium sulphate per liter of solution are given in the sixth and seventh columns. The curves plotted in the diagram are on the basis of the results given in the fourth and fifth columns, giving the

grams of each salt present in 100 grams of water at the various temperatures. These figures were selected simply because they yield a diagram which is not so crowded, and is, therefore, clearer than if the results were plotted on any other basis. The nature of the curves is in no wise different, and the peculiarities they present are as clearly seen as they would be if plotted on any other basis.

Table I.— *Temperature 10° C.*

Weight of 100 cc. of solution.	Grams NaCl per 100 cc. solution.	Grams Na$_2$SO$_4$ per 100 cc. solution.	Grams NaCl per 100 grams H$_2$O.	Grams Na$_2$SO$_4$ per 100 grams H$_2$O.	Gram-molecules NaCl per liter.	Gram-molecules Na$_2$SO$_4$ per liter.
107.98	0.00	9.04	0.00	9.14	0.000	0.641
108.28	4.19	6.28	4.28	6.42	0.722	0.445
110.18	9.25	4.59	9.60	4.76	1.593	0.325
114.98	15.04	3.83	15.65	3.99	2.590	0.271
116.38	20.16	3.67	21.82	3.97	3.473	0.260
119.23	24.89	3.75	28.13	4.15	4.288	0.266
120.72	27.04	3.89	30.11	4.34	4.552	0.276
121.73	28.70	4.08	32.27	4.59	4.944	0.289
122.34	29.82	4.19	33.76	4.75	5.137	0.297

Table II.— *Temperature 21°.5 C.*

Weight of 100 cc. of solution.	Grams NaCl per 100 cc. of solution.	Grams Na$_2$SO$_4$ per 100 cc. of solution.	Grams NaCl per 100 grams H$_2$O.	Grams Na$_2$SO$_4$ per 100 grams H$_2$O.	Gram-molecules NaCl per liter.	Gram-molecules Na$_2$SO$_4$ per liter.
116.37	0.00	20.46	0.00	21.33	0.000	1.450
116.95	8.51	14.54	9.05	15.48	1.465	1.030
119.85	15.96	12.54	17.48	13.73	2.750	0.889
121.41	18.49	12.34	20.41	13.62	3.185	0.875
124.34	22.93	13.27	26.01	15.05	3.950	0.941
124.37	23.40	12.74	26.53	14.44	4.031	0.903
124.43	24.46	11.80	27.74	13.39	4.214	0.836
124.35	27.39	9.33	31.25	10.64	4.719	0.661
124.34	27.83	8.99	31.80	10.28	4.794	0.637
123.48	28.21	7.41	32.10	8.43	4.860	0.525
121.86	29.66	4.16	33.69	4.73	5.110	0.295
121.20	30.18	2.45	34.08	2.77	5.199	0.174
119.72	31.34	0.00	35.46	0.00	5.399	0.000

Table III.—*Temperature 25° C.*

Weight of 100 cc. of solution.	Grams NaCl per 100 cc. of solution.	Grams Na₂SO₄ per 100 cc. of solution.	Grams NaCl per 100 grams H₂O.	Grams Na₂SO₄ per 100 grams H₂O.	Gram-molecules NaCl per liter.	Gram-molecules Na₂SO₄ per liter.
121.56	0.00	27.14	0.00	28.74	0.000	1.923
121.16	2.56	24.87	2.74	26.57	0.442	1.764
121.76	7.56	21.47	8.15	23.15	1.301	1.522
....	16.90	19.15	....	....	2.912	1.357
124.94	17.76	18.35	19.86	20.52	3.060	1.301
124.05	22.52	13.13	25.48	14.86	3.880	0.931
123.89	27.39	8.73	31.21	9.95	4.719	0.619
123.79	27.98	8.40	32.02	9.61	4.820	0.595

Table IV.—*Temperature 27° C.*

Weight of 100 cc. of solution.	Grams NaCl per 100 cc. of solution.	Grams Na₂SO₄ per 100 cc. of solution.	Grams NaCl per 100 grams H₂O.	Grams Na₂SO₄ per 100 grams H₂O.	Gram-molecules NaCl per liter.	Gram-molecules Na₂SO₄ per liter.
122.79	0.00	29.13	0.00	31.10	0.000	2.065
123.04	2.49	26.90	2.66	28.73	0.430	1.906
122.98	4.91	25.23	5.29	27.17	0.846	1.788
123.49	7.28	24.00	7.90	26.02	1.255	1.701
125.88	14.40	22.18	16.13	24.83	2.480	1.571
125.34	16.90	19.12	18.91	21.39	2.912	1.355
124.89	17.56	17.97	19.64	20.11	3.025	1.274
124.46	18.46	17.14	20.77	19.29	3.180	1.214
123.80	28.22	8.32	32.33	9.53	4.861	0.590

Table V.—*Temperature 30° C.*

Weight of 100 cc. of solution.	Grams NaCl per 100 cc. of solution.	Grams Na_2SO_4 per 100 cc. of solution.	Grams NaCl per 100 grams H_2O.	Grams Na_2SO_4 per 100 grams H_2O.	Gram-molecules NaCl per liter.	Gram-molecules Na_2SO_4 per liter.
128.09	0.00	36.41	0.00	39.70	0.000	2.580
128.16	2.23	34.84	2.45	38.25	0.384	2.469
128.44	5.07	32.98	5.61	36.50	0.873	2.337
129.02	7.09	32.25	7.91	35.96	1.221	2.287
127.63	9.52	28.39	10.61	31.64	1.640	2.017
127.03	11.04	26.68	12.36	29.87	1.901	1.891
125.76	13.99	22.37	15.65	25.02	2.411	1.586
124.90	16.48	19.04	18.44	21.30	2.839	1.350
124.39	18.40	16.97	20.66	19.06	3.170	1.203
123.58	28.32	7.91	32.43	9.06	4.878	0.561

Table VI.—*Temperature 33° C.*

Weight of 100 cc. of solution.	Grams NaCl per 100 cc. of solution.	Grams Na_2SO_4 per 100 cc. of solution.	Grams NaCl per 100 grams H_2O.	Grams Na_2SO_4 per 100 grams H_2O.	Gram-molecules NaCl per liter.	Gram-molecules Na_2SO_4 per liter.
132.89	0.00	43.38	0.00	48.48	0.000	3.075
132.30	1.09	41.64	1.22	46.49	0.188	2.951
131.78	1.79	40.44	1.99	45.16	0.308	2.866
131.47	2.37	39.50	2.64	44.09	0.408	2.800
130.86	3.11	38.17	3.47	42.61	0.536	2.705
126.50	10.86	26.21	12.14	29.32	1.871	1.858
123.68	19.45	15.31	21.87	16.83	3.351	1.085
123.42	28.62	7.64	32.84	8.76	4.930	0.541
121.68	29.84	4.07	33.99	4.63	5.140	0.288
120.80	30.54	2.41	34.77	2.75	5.261	0.171

Table VII.—*Temperature* 35° C.

Weight of 100 cc. of solution.	Grams NaCl per 100 cc. of solution.	Grams Na₂SO₄ per 100 cc. of solution.	Grams NaCl per 100 grams H₂O.	Grams Na₂SO₄ per 100 grams H₂O.	Gram-molecules NaCl per liter.	Gram-molecules Na₂SO₄ per liter.
132.36	0.00	42.89	0.00	47.94	0.000	3.040
131.37	1.93	39.39	2.14	43.75	0.333	2.792
125.61	12.19	23.59	13.57	26.26	2.099	1.711
123.77	16.78	17.64	18.78	19.74	2.891	1.250
123.08	28.47	7.39	31.91	8.28	4.905	0.524
119.30	31.34	0.00	35.63	0.00	5.399	0.000

DISCUSSION OF RESULTS.

From Mulder's[1] results on the solubility of sodium sulphate, quoted in Comey's "Dictionary of Solubilities," page 452, it appears that the figure given for the solubility of sodium sulphate at 21°.5 is somewhat too low. Mulder found that at 21°.5 C. there was contained 21.7 parts of sodium sulphate per 100 parts water, while the results here show only 21.33 parts. This difference is possibly due to an error in the temperature observation in the present case. It appears that at 21°.3 C. Mulder obtains the same figures that are given here for 21°.5, consequently it may well be that the temperature at which the work here described was done may have been 21°.3 instead of 21°.5. The thermometer used was graduated only to whole degrees, and moreover had not been calibrated, so that such an error might easily be thus accounted for. Similarly, for the results obtained at other temperatures, a correction may be applied by comparing with Mulder's results, and there would be obtained 25°.4 instead of 25° C., 26°.5 instead of 27°, 29°.6 instead of 30°, 32°.25 instead of 33°. For 35°, however, a similar correction cannot well be allowed, since Mulder finds for 35°, 50.2 parts dissolved against only 47.9 in the present case.

An inspection of the diagram will show that there are present two distinct classes of curves, one class representing re-

[1] "Scheikundige Verhandelingen Onderzoekingen," edited by Mulder, Rotterdam, 1857-64. The original is not accessible to me.

sults obtained above 33° C., consisting of pairs of curves with one intersection as required by the phase rule; the other class representing results obtained at temperatures below 33°, showing three curves in each case, with two points of intersection.

To account for the peculiarity in the nature of the curve

Grams NaCl per 100 grams H₂O
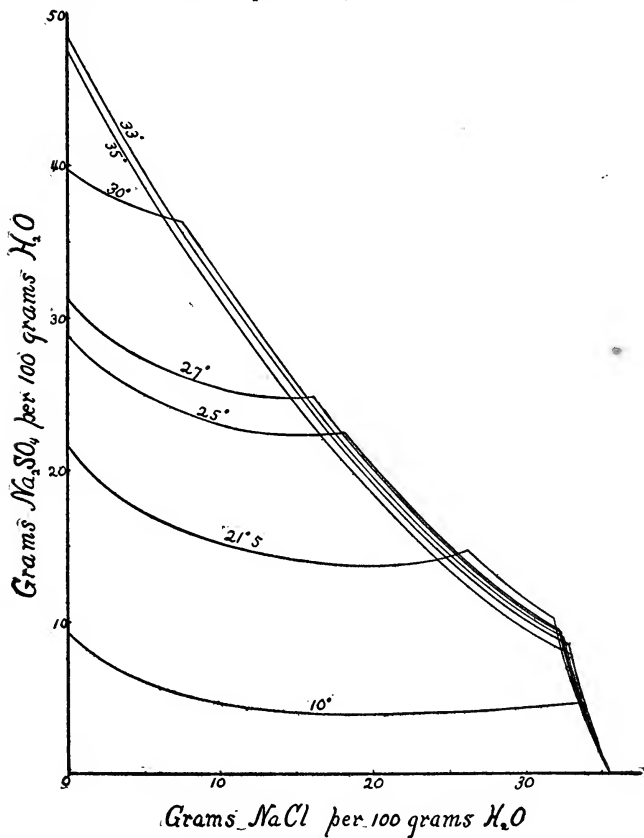
representing the mutual solubility of these two salts in solutions of each other, it is necessary to remember the peculiarity exhibited by sodium sulphate in regard to its solubility alone in water at various temperatures. It is well known that at about 33° sodium sulphate changes from its characteristic ten hydrate crystalline form to the anhydrous salt. Consequently at this temperature, and above, the curves represent the solubilties of two, simple, non-isomorphous, anhydrous salts, sodium sulphate and sodium chloride, with one homogeneous solid phase, except at one point, the point of intersection. This behavior is in strict accord with the phase rule, and the cases described here appear to be perfectly normal.

Below 33°, however, a different state of affairs exists, as will be seen by referring to the diagram. The solubilities of various mixtures for any given temperature below 33° and above a temperature in the neighborhood of 17° C. are seen to be expressed by *three* curves intersecting in *two* points.

The lowest curve representing the solutions in which sodium chloride is present in excess, lie close to, and present the same general features as those curves representing the same mixtures at higher temperatures. The middle curve in each case is practically parallel to the curves obtained at higher temperatures when the solutions were in contact with solid anhydrous sodium sulphate. And, as will be presently pointed out, the solid phase controlling these middle curves is in fact the anhydrous salt, notwithstanding that they represent conditions existing below 33°.

The upper curve is the normal solubility curve for the decahydrate of sodium sulphate in solutions of sodium chloride. As will be seen from the diagram, the general nature of the solubility curve for the decahydrate is quite different from that for the anhydrous salts. And, certainly, at the lower temperatures it presents the unusual feature of a minimum point. At a temperature below 17°, the solid phase in contact with the solution is probably the heptahydrate. One curve, for 10° C., was determined, and as the diagram shows, it is entirely similar to the solubility curve for the decahydrate.

Considering further the course of the curves obtained at

temperatures below 33°, it is seen that in each case as the original direction of these curves causes them to come into the region of the curves for anhydrous salt (that is, the curves for 33° and above), the direction of the former is changed and becomes parallel to the latter curves, itself a strong argument for the view that the solid phase in contact with the solution was the same in all such cases, *i. e.*, the anhydrous sodium sulphate. If the curves for the decahydrate continued their direction, and crossed the curves for the anhydrous salt in order to meet the line representing the solubility of sodium chloride in sodium sulphate extended, it would mean that solutions would be obtained which would be supersaturated with respect to the anhydrous sodium sulphate. In order that the solution could have been supersaturated with respect to anhydrous sodium sulphate, it would be necessary that none of the solid anhydrous salt should be in contact with the solution. The temperature being below 33° would ordinarily insure the presence of no anhydrous sodium sulphate, consequently it is to be expected that such points in the field beyond the 33° curve should be obtained. In no case, however, were they realized, and we are again led to the conclusion that anhydrous sodium sulphate was really in contact with the solutions even at temperatures below 33° C., and thus that an inversion of the decahydrate to the anhydrous salt takes place at various temperatures below 33°, depending upon the amount of sodium chloride contained in the solution in contact with the solid sodium sulphate.

In order to more satisfactorily demonstrate this the following experiment was performed: Two test-tubes, each containing a thermometer, were immersed in a large beaker of water. In the first test-tube was placed a saturated solution of sodium sulphate and also several large, well-formed crystals of the decahydrate. In the second test-tube was placed a solution saturated with respect to both sodium chloride and sodium sulphate, and also several large, well-formed crystals of the decahydrate. The temperature of the water in the beaker was slowly and gradually raised. At about 28° the crystals of the decahydrate in the second test-tube began to

cloud and become opaque around the edges, and as the temperature was maintained constant, this process continued until the whole mass was completely transformed from clear, translucent crystals of the decahydrate to an opaque mass of anhydrous salt. The crystals in the first test-tube remained unaltered. Thus it seems quite evident that the transformation of the decahydrate to anhydrous sodium sulphate at temperatures below 33°, is quite possible when the crystals are in contact with concentrated solutions of sodium chloride.

The change in the inversion temperature at which the decahydrate goes over to the anhydrous sodium sulphate, in the presence of a third substance in solution, which has just been described, is analogous to another case which has received attention in this laboratory. Van't Hoff and Armstrong,[1] Vater,[2] and Zunino[3] have recently called attention to the fact that gypsum, the dihydrate of calcium sulphate, was transformed to the hemihydrate at various, widely differing temperatures, depending upon the nature of the solution with which it was in contact. Cameron,[4] I believe, was the first to call attention specifically to this point. He investigated this case experimentally by a method similar to the one described in this paper, using a number of solutions of various salts, and various liquids. The facts brought out in this paper strengthen the view put forward regarding this phenomenon, and indicate the probability of its being found again in future studies of this nature.

In conclusion, I wish to acknowledge the assistance and advice of Dr. Frank K. Cameron, in carrying out this investigation and in the interpretation of the results.

[1] Sitzungsber K. Preuss. Akad. Wiss., **28**, 559 (1900).

[2] *Loc. cit.*, **28**, 269 (1900).

[2] Gazz. chim. ital., **30**, 1, 333 (1900).

[4] Bulletin 18, page 37, Division of Soils, U. S. Department of Agriculture.

ON THE PREPARATION OF BROMOFORM BY ELECTROLYSIS.

By Paul Coughlin.

In 1884 E. Schering took out a patent (D. R. P. 29771) for the preparation of iodoform, bromoform, and chloroform by electrolysis. The patent specified that the respective halogen salts of the alkalies or alkali earths should be electrolyzed in the presence of alcohol, acetone, or aldehyde in a warm aqueous solution. Carbon dioxide was to be passed continuously into the electrolyte during the electrolysis.

Elbs and Herz,[1] in 1897, published the results of their investigation of the process covered by this patent in regard to the preparation of iodoform from alcohol and acetone. In regard to the preparation of bromoform they say : '' Equally unsuccessful'' (referring to their lack of success with acetone) '' was an experiment on the electrolytic preparation of bromoform, in which the anode solution consisted of 6 grams soda and 10 grams potassium bromide in a mixture of 20 cc. alcohol and 100 cc. water ; the anode density was 0.5 ampere per square decimeter ; the temperature 60°. After 1.5 ampere hours the solution contained no bromoform.''

I repeated the foregoing experiment with the same result that they obtained. Replacing the sodium carbonate by caustic soda did not change the result, nor was it changed when acetone was used instead of alcohol, and the two experiments repeated.

Having found previously that a temperature of 75° was necessary to obtain the best yield of iodoform from alcohol, I tried this temperature in preparing bromoform from alcohol and acetone. In order to maintain this temperature the electrolytic cell was placed in a water-bath, and to prevent loss of acetone or alcohol by evaporation the anode compartment —a porous cup—was fitted with a reflux condenser. The experiments with alcohol and carbonate, alcohol and caustic,

[1] Ztschr. Elektrochem., 4, 4, Aug. 20, 1897.

acetone and carbonate, and acetone and caustic, were repeated at 75° and then at 95°, but all resulted negatively.

The concentration of the solution was varied, and then the proportions of the various substances in the electrolyte, but without success. In many of these experiments an exceedingly penetrating, highly disagreeable odor showed the formation of brom acetones. To prevent this as much as possible, the acetone (or alcohol) was allowed to run into the electrolyte gradually during the electrolysis. Several of the former experiments were repeated with this modification, but in no case could any bromoform be detected.

The next attempt was with the electrolyte at room temperature. The electrolyte was 10 grams potassium bromide and 15 grams sodium carbonate in 75 cc. water and 20 cc. acetone, the anode and cathode being separated by a porous cup. A small drop of bromoform resulted from this electrolysis.

Having succeeded in obtaining a small yield of bromoform I endeavored, by systematic variation of the conditions that might affect the yield, to increase it to the maximum.

In all the following experiments the apparatus used consisted of a beaker of 250 cc. capacity in which was suspended a porous cup of 110 cc. capacity. The porous cup was made the cathode chamber, and in this was put a solution of 10 grams sodium carbonate in 100 cc. water ; the cathode was an iron-wire gauze of about 60 sq. cm. superficial area on a side. The beaker contained the anode solution and the anode of platinum foil which had an area of 50 sq. cm. on each side. Usually two of these cells were connected in series, and in every case a copper voltameter was put into the circuit. Except when temperature conditions were tried, the cells were placed in vessels of cold water, so that the temperature varied but little from 25°. The time of the experiments was so varied that the amount of current used might be approximately the same for each experiment.

The formation of bromoform from acetone is expressed by the following equation :

$$6Br + (CH_3)_2CO + H_2O = CHBr_3 + CH_3COOH + 3HBr.$$
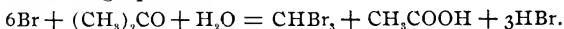
The presence of acetic acid in the electrolyte could readily be detected by the ethyl-ester test.

The bromoform was measured by being washed into a graduated tube and centrifugalized. The weight was found by considering the specific gravity to be 2.8. After some quantity had been collected, 10 cc. was distilled and practically all passed over between 140° and 155°.

In the first experiments the acetone was added to the electrolyte in equal quantities at intervals of ten minutes during the electrolysis, and the effect of varying the amount of sodium carbonate was tried; caustic soda was then substituted for the carbonate. The results are shown in the following table:

No.	KBr. Grams.	Acetone. cc.	Water. cc.	Caustic. Grams.	Carbonate. Grams.	Anode density. Amp. per sq. cm.	Voltage.	Temperature.	Time. Hours.	Ampere hours.	Yield. Grams.	Yield. Per cent of theory.
1	12	12	90		1	2.2	11.2	25°	2	2.2	0.7	19
2	12	12	90		5	2.2	9.5	25	2	2.2	0.4	11
3	12	12	90		2	2	4	25	2	2	1	30
4	12	12	90		3	2	4.5	25	2	2	1.1	33
5	12	12	90	1	2		11.2	25	2	2	0.3	9
6	12	12	90	2	2		5	25	2	2	drop	2
7	12	12	90	5	2		9.5	25	2	2	0.0	0
8	12	12	90	0.1	2		4	25	2	2	1.2	36

At the end of the electrolysis, in each case where the yield was very large, the electrolyte was colored by free bromine and had to be treated with caustic alkali or carbonate to free the bromoform of bromine. The limit of the yield with these conditions was soon reached; an experiment in which all the acetone was added at the beginning of the electrolysis showed the same yield that was obtained when the acetone was added gradually.

The fact that the yield decreased when enough carbonate was added at the beginning to keep the electrolyte clear, and that otherwise free bromine was present, suggested that it would be better to add the carbonate at intervals. When this was done a marked increase in the yield was shown. In the succeeding experiments the carbonate was added at such a rate that the electrolyte remained barely colored by free bromine. In some of the first experiments the carbonate was added in solution, but later, that the electrolyte might remain at constant volume, the solid was used with the same result.

5-27

The effect of temperature on the yield is shown by the following tables, the first having been made before the other conditions necessary to a maximum yield had been discovered :

No.	KBr. Grams.	Acetone. cc.	Water. cc.	Carbonate. Grams.	Anode density. Amp. per. sq. cm.	Voltage.	Temperature.	Time. Hours.	Ampere hours.	Yield. Grams.	Yield. Per cent of theory.
9	12	15	90	3	2.3	4.5	5°	2	2.3	2.0	53
10	12	15	90	3	2.3	4.3	15	2	2.3	2.1	55
11	12	15	90	3	2.3	4.3	25	2	2.3	2.24	59
12	12	15	90	4	2.3	4.2	35	2	2.3	1.54	40.8
13	25	10	75	6	3.8	5.5	10	1 : 15	2.37	3.08	82
14	25	10	75	6	3.8	5	15	1 : 15	2.37	3.64	97
15	25	10	75	6	3.8	4.3	20	1 : 15	2.36	3.7	99
16	25	10	75	6	3.84	4.2	25	1 : 16	2.4	3.8	100
17	25	10	75	6	3.8	3.8	30	1 : 15	2.36	3.73	100
18	25	10	75	6	3.6	3.8	35	1 : 20	2.37	3.4	90
19	25	10	75	6	3.85	3.8	40	1 : 15	2.4	3.08	81
20	25	10	75	6	4.0	3.5	50	1 : 10	2.4	3.08	81

Current density is a considerable factor in determining the yield, but in a modified way. This is seen by the following table. The first four experiments were made using a platinum gauze of 50 sq. cm. superficial area on a side, or a total of about 100 sq. cm. In the last four, the foil 5 x 10 cm. was used. These experiments would seem to indicate that the amount of current in proportion to the volume of the electrolyte has much to do with the result :

No.	KBr. Grams.	Acetone. cc.	Water. cc.	Carbonate. Grams.	Anode density. Amp. per. sq. cm.	Voltage.	Temperature.	Time. Hours.	Ampere hours.	Yield. Grams.	Yield. Per cent of theory.	
21	25	10	75	6	0.8	3.5	25°	2 : 18	1.9	2.52	84	Gauze 100 sq. cm.
22	25	10	75	6	1.3	4.9		1 : 36	2.1	3.3	100	
23	25	10	75	6	1.8	4.5		1 : 15	2.3	3.64	100	
24	25	10	75	6	2	5		1	2.1	3.0	91	
25	25	10	75	6	1.6	3.5		2 : 18	1.9	2.38	79	Foil 4 x 10 cm.
26	25	10	75	6	2.6	4.3		1 : 36	2.3	3.22	97	
27	25	10	75	6	3	4.5		1 : 30	2.3	3.64	100	
28	25	10	75	6	3.6	4.8		1 : 15	2.3	3.36	92	

A great many experiments had been tried, using only a little more than the theoretical amount of potassium bromide before the effect of increasing this amount was tried ; but the maximum current efficiency was attained only when this amount was doubled, as shown below. The table shows that there is a definite maximum in this case, for when a greater amount of potassium bromide is added the yield decreases :

No.	KBr. Grams.	Acetone. cc.	Water. cc.	Carbonate. Grams.	Anode density. Amp. per. sq. cm.	Voltage.	Temperature.	Time. Hours.	Ampere hours.	Yield. Grams.	Yield. Per cent of theory.
29	10	10	75	6	3.6	4.2	25°	1 : 15	2.3	3.22	89
30	15	10	75	6	3.2	4.3		1 : 30	2.4	3.5	92
31	25	10	75	6	3.8	4.2		1 : 15	2.4	3.8	100
32	30	10	75	6	3.2	4.2		1 : 30	2.4	3.5	92
33	35	10	75	6	3.6	4		1 : 15	2.3	3.08	84

In the case of acetone, as of potassium bromide, the maximum current efficiency could not be attained when only the theoretical amount was used. The table shows, however, that the yield in regard to the amount of acetone was greatest when only the theoretical amount was used. The greater part of the excess of acetone remained unchanged in the electrolyte.

No.	KBr. Grams.	Acetone. cc.	Water. cc.	Carbonate. Grams.	Anode density. Amp. per. sq. cm.	Voltage.	Temperature.	Time. Hours.	Ampere hours.	Yield. Grams.	Yield. Per cent of theory.
1	25	1.5	75	6	3.6	3.8	25	1 : 20	2.37	0.84	22
2		2.5	75	6	3.6	4.3		1 : 15	2.3	1.12	31
3		5	75	6	3.6	4.6		1 : 15	2.3	2.24	62
4		7.5	75	6	3.7	4.3		1 : 15	2.36	3.08	82
5		10	75	6	3.8	4.2		1 : 16	2.4	3.8	100
6		15	75	6	3.8	4.8		1 : 16	2.4	3.88	100
7		20	75	6	3.7	5		1 : 15	2.36	3.73	100

In a few experiments in which alcohol was used instead of acetone, only a small amount of bromoform was formed. In

no case was the current yield greater than 10 per cent of theory.

ELECTROCHEMICAL LABORATORY,
INDIANA UNIVERSITY,
May 25, 1901.

NOTE ON THE RATE OF HYDRATION OF META-PHOSPHORIC ACID.

BY J. C. AND F. C. BLAKE.

It is well known that a water solution of metaphosphoric acid slowly changes to either pyro- or orthophosphoric acid at the ordinary temperature, according to the amount of water present. The rate of this change was investigated by Sabatier,[1] who employed the methods of acidimetry. We have reinvestigated the same reaction according to one of the methods recently outlined by Duane.[2] In his words: "In this
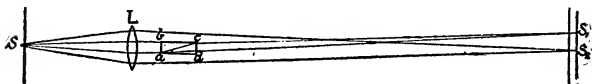

Fig. I.

method the basis of the measurement is the change in the index of refraction of the system, and it is applicable to those chemical systems only that are transparent. It is substantially the following: Rays of light from an illuminated slit S (Fig. I), passing through a long-focus lens L and the tube $a\,b\,c\,d$ form a distant image S_1 of S. The slit S is perpendicular to the plane of the diagram, which represents a horizontal section of the apparatus. The tube $a\,b\,c\,d$ has plane glass ends $a\,b$ and $c\,d$, and a plane glass plate $a\,c$ divides it into two wedge-shaped compartments. The ends $a\,b$ and $c\,d$ are not quite parallel to each other, so that if the two compartments are filled with liquids having the same index of refraction there will be a slight resultant refraction of the light rays that pass through the tube. The rays of light that pass outside of the tube will, therefore, form an image S_2 a little to

[1] Compt. rend., **106**, 63; **108**, 738, 804.
[2] Am. J. Sci., May, 1901.

one side of S_1. It is evident that if the liquid in one compartment (the wedge $a\,c\,d$ for instance) is undergoing a chemical change its index of refraction in general will vary and the image S_1 will move sideways. The distance that S_1 has moved will be a measure of the change that has taken place in the index of refraction and, therefore, of the amount of substance in $a\,c\,d$ that has reacted. The displacements of S_1 can be determined by comparing its distances from S_2 which remains stationary.

" In order to obtain a complete record of the position of S_1 a photographic plate, $S_1\,S_2$, is placed in a vertical position at the images S_1 and S_2, and just in front of it is a screen. A narrow horizontal slit cut in the screen allows a small part of the light only to pass through. At any instant of time, therefore, there will be two small spots of light on the plate at the intersections of the two vertical images S_1 and S_2 with the projection of the slit on the plate. A system of cog-wheels allows the photographic plate to fall slowly during the reaction, so that two lines are drawn on it—one of them straight, due to the fixed image S_2, and the other curved, due to the moving image S_1. The curved line represents the reaction, in that the abscissas are proportional to the intervals of time and the ordinates represent (but are not proportional to) the quantities of the substance that have reacted. After the reaction is completed, the plate is drawn up and allowed to run down again, the image S_1 now tracing another line that is practically straight. This line may be taken as the zero line [the axis of x], and the distances between it and the curved one are (at least in some cases) proportional to the amounts of the original compounds left in the solution [at the corresponding times]."

Practically, the applicability of the method is quite limited, owing to the conditions of the experiment. The refractometer is a convenient instrument to use in determining whether the change in the index of refraction of any given system be sufficiently large to yield good results (methyl acetate and water were rejected on this account), as well as to ascertain approximately the necessary strength of the solution. Of

course, no ingredient can leave the field in the form of a gas or a precipitate. The use of a catalytic is permissible. The method would seem to be especially serviceable for those reactions whose constituents may hardly be gauged by chemical methods, such, for example, as those involving molecular rearrangement.

A suitable reaction having been decided upon, a measured amount of the solution is allowed to react completely and is then placed in one end of the tube. The same amount of a fresh solution is then mixed, and the clockwork started at the same instant. The position of the plate while at rest was recorded by a flash-light, whereby an image of the horizontal slit was photographed on the plate, which corresponds in position to the ordinate at the beginning of the reaction (the axis of y). The fresh solution is then placed in the other end of the tube, and, after adjusting the focus, the plate is exposed. It might be of practical importance to add that considerable difficulty was experienced in adjusting the focus, due to the fact that the fresh solution just introduced into the tube is not entirely homogeneous, especially where it comes in contact with the glass to which traces of the former solution always adhere. If the focus is not readily adjustable, so much of the best part of the curve is lost that the plate is practically worthless. Therefore, after many failures, the following method was adopted : Place in each end of the tube a solution that has already reacted and adjust the lens so that the beam through the solution will be in focus on the plate. If this causes the side-light to blur too much to give a distinct image at S_2, a separate lens or a separate source of light will have to be introduced for this purpose. A fresh solution is then introduced into one end of the tube and the plate exposed. It will usually appear to the eye that the beam through the solution is no longer in focus ; but experience teaches that it will, nevertheless, make an impression on an '' extra-sensitive'' plate as a fine line, becoming even finer as the fresh solution becomes more homogeneous. The plate herewith represented is not one of the best so far as the focus is concerned, but the improvement in this respect may readily be observed.

We call attention to the following precaution : After having been once set up the apparatus must remain absolutely fixed, not only during the few days necessary to complete one reaction, but during the time necessary to complete the whole series of reactions, especially those of the whole solution and the corresponding partial solutions. The ordinary precautions are not sufficient to guard against this source of error, since the plan of the apparatus is such that the slightest motion of the slit, the lens, or the tube, is magnified many times on the plate. Many plates were spoiled owing to this source of error without apparent explanation. In order that two plates may be comparable, the line traced by the side-light on the one must overlie the corresponding line on the other when the plates are superimposed, in order to show that the vertical slit and the lens have not been moved ; the line traced by the beam through the solution after the reaction is completed (the axis of x) on the one must overlie that of the other, in order to prove that the tube containing the solution has not been moved sidewise or turned about a vertical axis, and in order to prove that the two fresh solutions were of the same strength (this applies especially to partial solutions) ; and, of course, the side-light on any one plate must be represented by only a single line, no matter how many times the plate has been exposed, in order to prove further that the plate has not been moved.

In working with metaphosphoric acid, owing to the remarkable deliquescence of the substance, each specimen of the acid had to be prepared afresh and the weighing could be accomplished with only approximate exactness. One specimen, prepared by dissolving the anhydride in water and heating in a platinum crucible until the liquid remained quiet over an ordinary Bunsen burner except for the escape of white fumes, contained 99.1 per cent of metaphosphoric acid ; although other specimens may have contained an amount of phosphorus corresponding to more than 100 per cent of metaphosphoric acid, as is usually the case, owing to the presence of anhydride. The customary difficulty was experienced in obtaining an acid sufficiently free from alkalies to be freely soluble in water.

The plate figured herewith represents the curve obtained as above described when 4 grams of metaphosphoric acid were dissolved in 5 cc. of water at $18°.5$, the temperature being kept nearly constant until the reaction was over. About nine minutes were required for solution. The second line from the top is the record left by the side-light, showing that the apparatus was not moved. The other four horizontal lines are the record of the reaction during four successive nights, the lowest one representing the end reaction (the axis of x), it having been previously determined that the reaction is completed in four days. This was done by allowing the plate to run down a fifth night, the line thus traced being identical with the line traced the fourth night. That the reaction was completed in the time specified is further shown, though not with the same degree of precision, by the fact that the line for the fourth night and the line traced by the side-light are measurably parallel. The vertical line at the right was due to the flash-light and represents the position of plate at the beginning of the reaction (the axis of y). The distance between this line and the beginning of the principal curve represents the time (nearly half an hour) necessary for introducing the solution into the tube and adjusting the focus. By having the focus pre-adjusted as indicated above, this interval was much reduced. The ordinates were drawn with the the dividing engine, and represent intervals of thirty minutes each.

Two lenses, L_1 and L_2, were used instead of one, L_2 being between the tube and the plate, and very near the tube in order not to neutralize the dispersion. The distance $S L_1 = 15.4$ cm.; $L_1 L_2 = 19.4$ cm.; $L_2 S_2 = 214$ cm.; $a b = 0.4$ cm.; $a d = 5.6$ cm.; $L_1 a = 5.8$ cm.; $d L_2 = 8$ cm. The width of the vertical slit S was 0.05 mm.; the width of the horizontal slit in front of the plate was 0.2 mm., and its distance from the plate was 0.6 cm. In order to improve the focus still further, the ends of the tube were covered with a black cloth having a vertical slit 0.27 cm. in width. The width of this slit might advantageously be still further reduced. The source of light was an ordinary incandescent electric bulb.

PLATE I.
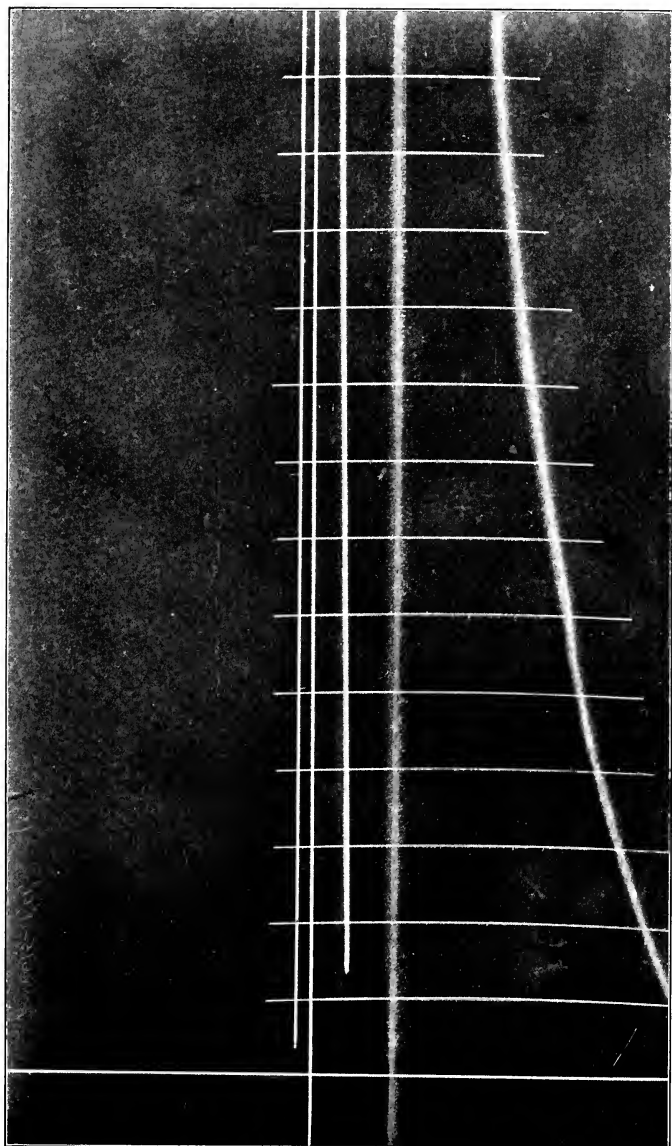
In the paper last referred to, it is presumed that in most cases the amounts of the original substances remaining unchanged at any given time will be directly proportional to the corresponding ordinate of the curve thus obtained ; that is, that this curve should fulfil the conditions of Guldberg and and Waage's law, that the rate at which the reaction proceeds is proportional to the amount of unchanged substance left in the solution. The foregoing assumption was to be proved, however, by placing in one end of the tube a mixture containing known amounts of new and old solution, and ascertaining whether the largest ordinate so obtained bore the same ratio to the largest ordinate obtained for a wholly fresh solution that the amount of fresh acid in the mixture bore to the amount of acid in the wholly fresh solution. For a solution of metaphosphoric acid so mixed, containing equal amounts of new and old solution, the largest ordinate was found to be only 40 per cent of the largest ordinate of the corresponding whole solution, or four-fifths of what it should have been to uphold the assumption. Several series of such plates have been obtained, checking as closely as might be expected (within 1 per cent) at 40 per cent. Therefore, as the curve photographed does not bear the simple relation above mentioned, it will be necessary to determine the ratio of the ordinates of the curve photographed to the amounts of fresh acid in the solution for several points by mixing new and old solutions in various known proportions, and from the points thus located to plot the curve that really corresponds to the amounts of metaphosphoric acid remaining unchanged at each instant of time. Since this has not been done and the apparatus has been taken down, it will be necessary to begin a new series of curves. Of course, no attempt can be made to determine the equation of the curve until this correction has been made. Owing to the force of circumstances, this cannot be undertaken for some time and we merely report progress. The previous work of Sabatier increases rather than diminishes the interest with which we await the opportunity to compare results obtained by methods so widely different.

We gratefully acknowledge our indebtedness to Dr. Wm. Duane for assistance and advice throughout the course of the work.

NOTES.

Radio-Lead.

In a note which appeared in the last volume of this JOUR-NAL,[1] attention was called to the important results obtained in the course of recent investigations on radio-active substances. Brief mention was made of the active lead salts obtained by Hofmann and Strauss[2] from a number of uranium minerals such as bröggerite, cleveite, pitchblende, alvite, samarskite, euxenite, and uranium mica. Since that time these authors have published the results of further investigations along the same line.[3] It now appears that these salts contain a new element closely related to lead.

By appropriate methods they are able to separate from the minerals, or from uranium residues, chloride of lead mixed with "radio-lead" chloride, and the chloride of still another new element which appears to be very closely related to ruthenium, as we should expect from its approximate atomic weight, 100.92. It is probably the homologue of manganese. It was not fully investigated.

From the more soluble portions of the mixed chlorides they obtained, besides the above-mentioned element, the strongly active radio-lead. Its sulphate was analyzed and found to contain about 41.7 per cent SO_4. If the metal be bivalent in the sulphate, this would indicate an atomic weight of 171.96, so that it might be regarded as the homologue of tin. Radio-lead can be precipitated from slightly acid solutions by hydrogen sulphide, its sulphate is insoluble in dilute sulphuric acid, its salts dissolve in caustic potash and can be precipitated by hydrogen sulphide. The nitrate is soluble in water, and from this solution it is almost completely precipitated by ammonium carbonate. Unlike lead, its chromate is not decomposed by sulphuric acid. Its chloride is more soluble than lead chloride, and its sulphide is at once decomposed by fuming hydrochloric acid. Lead sulphate gives a blue light when under the influence of the cathode rays ; radio-lead sulphate gives a bright-blue light and is afterwards phospho-

[1] This JOURNAL, **25**, 77 (1901).
[2] Ber. d. chem. Ges., **33**, 3126 (1901).
[3] *Ibid.*, **34**, 8, 907, 3033 (1901). See also Hofmann, Korn, u. Strauss : *Ibid.*, **34**, 407.

re scent. The active sulphate has an intense rose color when heated in the air to 500°. The chloride often has a similar color.

Radio-lead sulphate acts on the photographic plate through glass, aluminium, caoutchouc, paper, and air, and much more strongly than polonium obtained at the same time from the same minerals. It discharges the electroscope, but not as rapidly as polonium salts. Even when exposed to direct daylight for two months there was no change in its photographic activity. From this and from its action through aluminium it differs from the phosphorescent sulphides of the alkaline earths. The sulphate emits Becquerel rays. It was shown that radium and polonium purposely mixed with lead salts could easily be separated by the method used in preparing radio-lead sulphate, and the resulting lead sulphate was inactive. Further, radio-lead is unlike radium, polonium, and actinium in that its sulphate alone acts photographically. The sulphide, chloride, iodide, chromate, carbonate, and oxide made from strongly active sulphate are inactive, but regain their power when changed back into the sulphate. Since the activity ceases after some months it is evident that radium is absent. The renewal of activity under the influence of the cathode rays shows that polonium is not present. When the sulphate is partly changed into sulphide by heating with sulphur, it becomes inactive. The activity is greatly increased by heating to 450° for fifteen hours, and also by evaporating with sulphuric and nitric acids.

It was found that the sulphate, sulphide, chloride, iodide, chromate, and carbonate are alike in their action on the electroscope.

When equal amounts of radio-lead sulphate and of lead sulphate containing radium were placed on the glass side of a photographic plate it was seen that the radium had acted on the farther side of the gelatin layer, but the radio-lead acted only on the side next to the glass.

Since only the sulphate acts photographically while all the salts discharge the electroscope, it is evident the photographic radiation is not the same as that which produces the latter effect. Having in mind the latest work on thorium radiation and the discharge of electroscopes in the higher strata of the air, one might imagine that a tenuous, almost imponderable, substance adheres to radio-active substances, and by its gradual escape discharges the electroscope, and, secondarily, produces photographic effects. But this is not in agreement with the fact that heating to 450° increases the radio-activity.

It is probable that there is within the atoms some activity that causes the emission of rays of different wave-lengths, and, consequently, of different properties. It was at first thought that the activity might be due to positive charges due to the cathode rays. If this were the case, the anode rays should destroy this effect, but it was found that they produced a slightly greater activity. Neither can they be cathode rays, for they penetrate glass or a layer of air 1 cm. in thickness without appreciable weakening of effect.

This work of Hofmann and Strauss has been severely criticized by Giesel,[1] who first pointed out that it would be very difficult to obtain new radio-active substances in pure condition from such small quantities of the earths as 100 grams. He was of the opinion that the effects noticed must be due to the presence of very small quantities of the intensely active substances already known, or else to induced activity. More recently[2] he takes up the discussion anew, and repeats the experiments with two samples of radio-lead sulphate prepared by Hofmann and Strauss. His results are, in some respects, in direct contradiction to theirs. He finds that " the sulphate does not lose its Becquerel-radiation in three-fourths of a year, and it is not caused to give new or increased Becquerel-radiation by the cathode rays. All the compounds, and not the sulphate alone, act on the photographic plate. The apparently contradictory result of Hofmann and Strauss is explained by their arrangement of the experiment which does not exclude a secondary action of phosphorescent light. Radio-lead sulphate emits a mixture of Becquerel rays and light rays which are produced constantly by the former." When the plate is wrapped in black paper the action of the light rays is prevented and on long exposure the Becquerel rays finally act. Radio-lead sulphate and the carbonate, chloride, and sulphide prepared from it produced exactly the same effect under these conditions. He was able to detect a very faint phosphorescence in the sulphate.

Hofmann and Strauss found that the radio-lead rays acted on the bromide of silver layer on the side next to the glass, but the radium rays acted on the farther side. This is due to the fact that the light rays from the radio-lead sulphate are not able to penetrate the sensitive film as readily as the Becquerel rays.

Repeating the experiment of mixing radium and lead salts and then separating the two, he obtained an active lead sulphate

[1] Ber. d. chem. Ges., **33**, 19, 3569 (1900).

[2] Ber. d. chem. Ges., **34**, 3772 (1901).

in which radium could not be detected chemically. This was done by allowing the mixed solutions to stand for eight days before the separation. This was analogous to his previous experiments with bismuth.[1] The sulphide of lead so obtained, and the iodide made from it, were both active. He is of the opinion that Hofmann and Strauss have not yet proved the existence of a new radio-active element in radio-lead.

The new unnamed substance,[2] which acts chemically like lead and was discovered in uranium mother-liquors, shows no diminution of its intense activity after standing a year. In this respect it resembles radium and actinium. Polonium material shows a slight activity after two years. Fresh preparations lose their activity rapidly, but the rate of loss continually decreases, especially if the polonium be mixed with a large proportion of lead chloride.

He was able to show that the water of crystallization distilled from radium barium bromide is strongly active. That this is not due to radium carried over with the steam is shown by its loss of activity after a few days. Nearly all colorless or slightly colored solids became luminous under the influence of the radium rays, and the same is true of liquids such as water, and especially petroleum. The luminous zone does not extend far into the liquid.   C. E. W.

On the Existence of Ammonium.

The evidence in favor of the metallic nature of ammonium was summed up in a note in the first volume of this JOURNAL.[3] Le Blanc's work on ammonium amalgam formed by the electrolysis of ammonium salts at a low temperature seemed to have "removed the last experimental evidence against the metallic nature of ammonium." Quite recently Otto Ruff[4] attempted to obtain ammonium by the electrolysis of ammonium iodide dissolved in liquid ammonia. A tube, somewhat like an inverted Y with electrodes fused into the lower ends, was partly filled with potassium iodide. It was then cooled with liquid air and alcohol and dry ammonia was condensed in it. On passing an electric current through it iodine was set free at the positive pole, and at the negative pole were seen drops of a light, mobile, copper-colored liquid with a metallic appearance. These rose to the top and dissolved, forming a solution of an intense blue color. The substance was shown to be potassium ammonium, $K.NH_3$.

[1] Verh. d. phys. Ges., 5 Januar, 1900.
[2] Ber. d. chem. Ges., **33,** 19, 3570 (1900).
[3] This JOURNAL, **25,** 431 (1901).
[4] Ber. d. chem. Ges., **34,** 2604 (1901).

The electrolysis of ammonium iodide was next undertaken, but even when the solution was cooled down to its freezing-point, —95°, nothing but hydrogen was formed at the negative pole, and not a trace of blue color was seen in the solution. It was thought that some ammonium might be formed at high pressures, and the experiment was repeated with the upper end of the tube sealed, and the whole cooled to —95°. After the current had passed for five hours, and an estimated pressure of 60 atmospheres had been obtained, there was still no evidence of the formation of ammonium. There was also no ammonium amalgam formed when mercury was used as the cathode.

The author thinks that ammonium may possibly be obtained by working at still lower temperatures and with greater pressures. A suitable solvent for these conditions is unknown. Ammonium is not to be regarded as a true analogue of the alkali metals, but resembles the easily dissociated alkali-ammonium compounds such as $K.NH_3$, $Na.NH_3$, and $Li.NH_3$. It should be written $H.NH_3$ instead of NH_4.

<div align="right">C. E. W.</div>

REVIEWS.

There are few subjects in physical chemistry which are discussed more freely to-day than the phase rule, and few the meaning of which is less clearly understood. There are those persons who tell us that the phase rule is the one generalization of importance in physical chemistry, and that everything in physical chemistry, not to say in chemistry, should center around it.

On the other hand, there are those who will have very little to do with the phase rule even as applied to physical chemistry, and among this number can be mentioned some who stand in the very front rank of physical chemists.

The intermediate stage is, however, represented here as in so many other fields. Those who belong to this class regard the phase rule as an important generalization, which correlates a large number of more or less isolated facts already established, and which also suggests new lines of investigation. They regard the phase rule as one of the three or four impor-

tant generalizations that have been reached by modern physical chemistry, and upon which it is based. The author of the book in question belongs to this class.

It should be pointed out that much of the most important experimental work bearing upon the phase rule has been done by Roozeboom and his pupils. The book is, therefore, written by one whose knowledge of the phase rule has been applied in the laboratory.

The part of the book which is at hand deals only with systems containing one component. A brief historical introduction, including homogeneous and heterogeneous equilibrium, the phase rule, non-variant, mono-, di-, and polyvariant systems, is followed by a discussion of the various systems with one component. These include equilibrium between a liquid and a gaseous phase, equilibrium between a solid and a gaseous phase, equilibrium between a solid and a liquid phase, and equilibrium between two solid phases. The "triple-points" in the cases of solid, liquid and gas ; solid, solid, and gas ; solid, solid, and liquid ; and solid, solid, and solid, are considered at some length, and in such a clear and concise manner that the reader can scarcely fail to grasp their significance.

As far as one can judge of a book from the appearance of the first third of it, the work in hand is by far the clearest and most intelligible that has thus far been written on the phase rule. It is safe to predict that the completed work will contribute much to a better understanding of this important generalization, which has been frequently disregarded because of the unnecessary complexity in which it has been shrouded.

The second portion of the book will deal with systems of two components, and the third with three and more components.   H. C. J.

Jahrbuch der Elektrochemie, Berichte über die Fortschritte des Jahres 1900. Unter Mitwirkung der Herrn Prof. Dr. K. Elbs, Giessen, Prof. F. W. Küster, Clausthal, und Privat-docent Dr. H. Danneel, Aachen. Herausgegeben von Dr. W. Nernst, o. Professor an der Universität Göttingen, Direktor des Instituts für physikalische Chemie und Elektrochemie ; und Dr. W. Borchers, o. Professor an der Technischen Hochschule Aachen, Vorstand des Laboratoriums für Metallhüttenkunde und Elektrometallurgie. vii Jahrgang. Verlag von Wilhelm Knapp, Halle, A. S. 1901. pp. 596.

The "Jahrbuch der Elektrochemie" contains, as is well known, a brief survey of the work of the year in electrochemistry. This subject has two distinct phases, the scientific and the practical, and each has acquired the greatest prominence in the last few years. Each side of the subject is represented

by one of the ablest men of the day, and this insures a masterly treatment of the whole subject. The collaborators of Nernst and Borchers are men of high standing both in the science and application of chemistry.

For the convenience of those who use the book the material has been beautifully systematized. The scientific portion treats first of such general matters as lecture experiments, books which have appeared, description of methods, apparatus which has been devised, etc. The broad subject of conductivity is taken up and its applications to special problems, such as the dissociating power of solvents, the constitution of inorganic and organic compounds, the electrical conductivity of solids, and the like. One of the most interesting sections in this part of the work is that which has to do with electrolysis and polarization. The theory of electrolysis advanced by Le Blanc and now generally accepted, as well as his own beautiful investigations on polarization, have brought the whole subject very much to the front in the last few years. Since the work of Nernst on the electromotive force of primary cells, few investigations in the field of electrochemistry can be compared in importance with it, and this is shown by the amount of work done yearly in this field.

The material in applied electrochemistry is also well systematized under the general heads of production of electrical energy, electrolysis, including the production of the nonmetals, the metals, inorganic compounds, and organic compounds. This is followed by a discussion of forms of apparatus devised for use in applied electrochemistry.

The book is useful to all who are interested in any phase of electrochemistry, but especially to those who do not have access to the current literature of the subject.   H. C. J.

THE ELEMENTS OF QUALITATIVE ANALYSIS. By WM. A. NOYES, PH.D., Professor of Chemistry in the Rose Polytechnic Institute. Fifth edition, revised. New York : Henry Holt & Co. 1901.

Prof. Noyes' book is well known as one of the best brief laboratory manuals in use. In the present edition he has revised the scheme for the systematic detection of acids, employing in the main the methods suggested by Abegg and Herz.

A few pages of the introduction are given to a brief sketch of the theory of solutions.   E. R.

AMERICAN

CHEMICAL JOURNAL

XXXV.—THE ALLOYS OF LEAD AND TELLURIUM.

BY HENRY FAY AND C. B. GILLSON.

For several years past, investigations on the chemistry of tellurium have been carried on in the laboratory of this institution. The methods of preparation of pure tellurium[1] and the estimation of tellurium[2] have been studied, and an attempt to determine the atomic weight of tellurium is now in progress. All these problems had been investigated, however, along purely theoretical lines, and it was thought desirable to study the more practical application of the metal, which can now be had in considerable quantities as a waste product in the refining of copper ores. In its physical and chemical properties tellurium is very similar to antimony, and it was thought probable that it might replace antimony in certain alloys. Hence, it was decided to prepare and study the alloys of lead and tellurium.

Recently developed physico-chemical methods have thrown much light on the nature of solutions, and it has been shown that the properties of alloys are entirely analogous to those of solutions. The methods which have been of greatest service

[1] Norris, Fay, and Edgerly : This JOURNAL, 23, 105.
[2] Norris and Fay : *Ibid.*, 20, 278.

in studying the nature of alloys have been the determination of the fusibility curves, and the study of the structure by means of the microscope. These two methods give results which entirely corroborate each other. By the older methods of investigation, such as studies of the heat of formation, heat of solution, electrical conductivity, etc., the different methods not only did not give definite conclusions with regard to the constitution of the alloys, but, in most cases, led to different conclusions. The problem was undoubtedly much more complex than the study of ordinary chemical compounds, since in the latter case it was possible to use solvents which would not affect the nature of the substance when dissolved, whereas, for alloys, there was no solvent which would not entirely change the character of the substances. The work of Le Chatelier, Gautier, Heycock and Neville, Stead, and others has led, however, to definite conclusions, and the fusibility curves established by them have been found to be entirely analogous in character to the curves found for mixtures of simple chemical substances.

With the aid of the microscope the results obtained in the determination of the fusibility-curve have been confirmed. The microscope gives an approximate analysis of the different constituents contained in the alloy, and, in many cases, a clue to the order of solidification of the several constituents.

Various alloys composed of two metals have been found to give curves of fusibility, which fall under one of the three following classes, illustrated in the diagrams, Figs. I, II, and III :

1. Two metals which form solid solutions give a straight-line curve connecting the two freezing-points (see Fig. I.). Roozeboom[1] has shown that this curve may have a maximum or a minimum point, but these points may readily be distinguished, by means of the microscope, from maximum points representing compounds, and minimum points corresponding to eutectic alloys.

2. Two metals which form neither solid solutions nor compounds give a curve of two branches meeting in a eutectic,[2]

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[1] J. Phys. Chem., **30**, 385.

[2] The eutectic is that alloy, of definite composition and constant melting-point, in
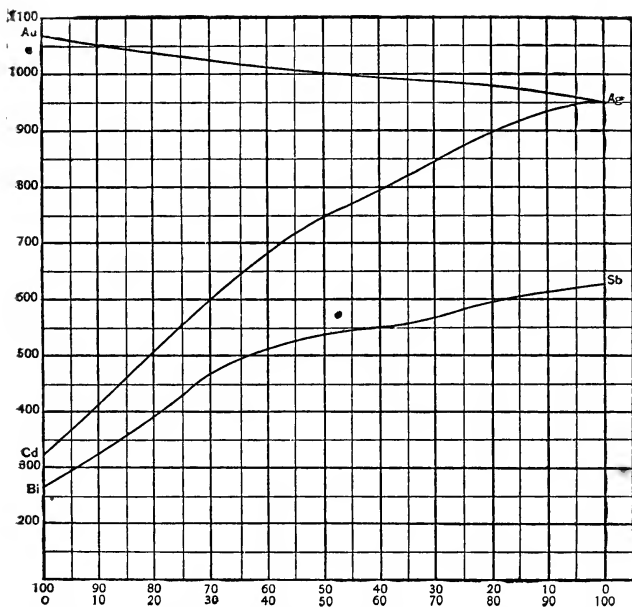
Fig. I.—Diagram showing melting-points of gold-silver, cadmium-silver, and bismuth-antimony alloys. (The ordinates represent degrees C.; the abscissae, percentages of the two constituents of each alloy.)

the freezing-point of which is lower than the freezing-point of either metal (see Fig. II.).

3. Two metals which form one or more compounds give a curve, the number of branches of which is dependent upon the number of compounds formed. In this class one of the compounds may form a solid solution with one of the pure metals, or with another compound (see Fig. III.).

The examples of these classes of alloys, together with their fusibility-curves, shown in Figs. I., II., and III., are offered,

which the constituents are in equilibrium at all temperatures. Its melting-point is lower than the melting-points of its constituents, and its composition is not altered during solidification. The eutectic alloy may be composed of two metals, two compounds, or two solid solutions; a metal and a compound, a metal and a solid solution, or a compound and a solid solution.

not as a complete summary of the work actually accomplished in this field, but merely to illustrate the nature of the work. Many of these curves have been plotted from Gautier's work,[1] and have not been experimentally confirmed.

In Fig. II. the minimum points correspond to the eutectic mixtures ; in Fig. III. the maximum points in the curves correspond to definite compounds, and the minimum points to the eutectic alloys.

The study of the microstructure of these three classes of alloys confirms very decisively the fusibility-curves. In the first class it is known that the solvent and dissolved substance separate out together. The microstructure of metals which form solid solutions shows a homogeneous mass, in which it is difficult, if not impossible, to distinguish between the two constituents. The alloys of gold and silver, cadmium and silver, and antimony and bismuth would show on microscopic examination to be composed of homogeneous mixed crystals of the two constituents. In the second class, where the freezing-point of the pure metal is considerably lowered by the addition of the other metal, we know that there is first a separation of pure solvent, and that, as the temperature of the solution is lowered, the pure metal continues to separate until the concentration of the resulting solution has reached that of the eutectic alloy, when the mass solidifies as a whole. The microscopic constituents, consequently, should be the pure metal and the eutectic—the amount of each depending upon the proportion of the two metallic constituents. As the eutectic is the alloy in which the two constituents are mutually saturated, and as the two separate simultaneously, we should expect to find a structure made up of alternate layers of the two metals. This is actually found to be the case, and the structure for all eutectics is very characteristic, resembling the fine-lined markings of the human thumb. The eutectic may consist of two metals, of metal and a compound, or of two compounds ; but in all cases its structure is very characteristic and easily recognized. This class of alloys may be illustrated by taking as an example the fusibility-curve of the tin-bismuth alloys, Fig. II. The branch of the curve be-

[1] Gautier : Bull. Soc. d'Encouragement, **1**, 1293 (1896).
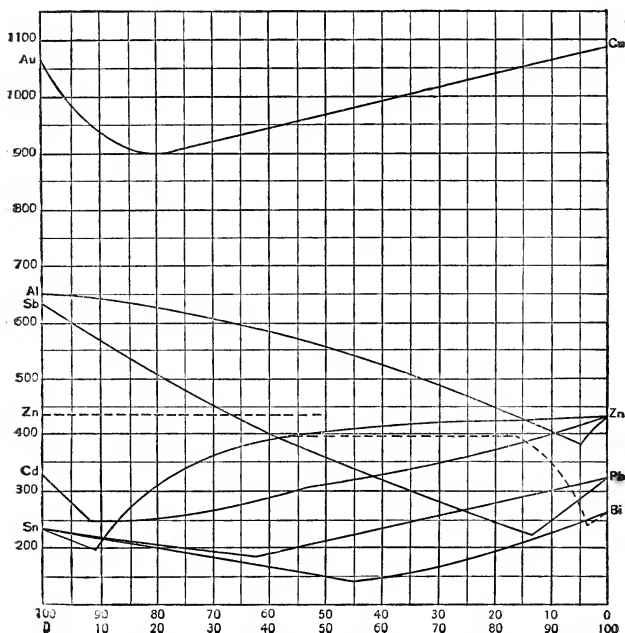
Fig. II.—Diagram showing melting-points of gold-copper, aluminium-zinc, antimony-lead, zinc-bismuth, cadmium-zinc, tin-zinc, tin-lead, and tin-bismuth alloys. (The ordinates represent degrees C. ; the abscissae, percentages of the two constituents of each alloy.)

tween 45 and 100 per cent of tin represents the separation of tin and the eutectic of tin and bismuth, the amount of each depending upon the composition. As, by increasing the percentage of bismuth, we approach the composition of the eutectic alloy, 45 per cent tin, more and more of the eutectic structure will appear until the whole mass consists of the eutectic alone. The additions of bismuth to tin have successively lowered its freezing-temperature until, at 55 per cent of bismuth, the lowest freezing-temperature has been reached, and both metals separate simultaneously from solution. With the further addition of bismuth, the freezing-temperatures begin

to rise, and the branch of the curve between 55 and 100 per cent of bismuth represents the separation of bismuth (which is now the solvent) and the eutectic alloy, the relative quantities of each being dependent upon the percentage composition. As the composition approaches that of the pure metal, there will evidently be an excess of the pure metal over the eutectic. The presence of compounds of the third class is usually recognized by their crystalline form, the forms of some of them being very characteristic, such as is the case for the compound $SnCu_3$. When, however, a compound forms a solid solution, the detection of the two constituents is much more difficult. To illustrate the third class of alloys we may take, as an example, the alloys of nickel and tin, giving a three-branch curve of fusibility, as determined by Gautier, which is nothing more than a combination of classes 1 and 2. The first class is represented in the branch of the curve between the maximum point at 67 per cent, corresponding to the compound NiSn, and 100 per cent of tin. The microscopic constituents between these two points consist of homogeneous mixed crystals of the compound NiSn and pure tin. The compound forms a eutectic alloy with nickel. Whether we consider the compound NiSn or pure nickel as the solvent, the freezing-point of each is lowered by addition to the other until they are mutually saturated. We then have the eutectic alloy, melting at the lowest possible temperature at which it is possible for a mixture of these two constituents to melt.

The microscopic constituents of the branch between 67 and 100 per cent of nickel consist of pure nickel and the eutectic of nickel and the compound NiSn; between 67 and 33 per cent of the compound and the eutectic.

The Preparation of Pure Tellurium.

The metallic tellurium required was extracted from the slime which is the waste product of the electrolytic process employed at the Baltimore Copper Works in the treatment of copper mattes from the West. This residue, after the removal of silver and copper, consists principally of the sodium salts of silicic, selenous, and tellurous acids, the last named being in large excess. The process by which the necessary liquid
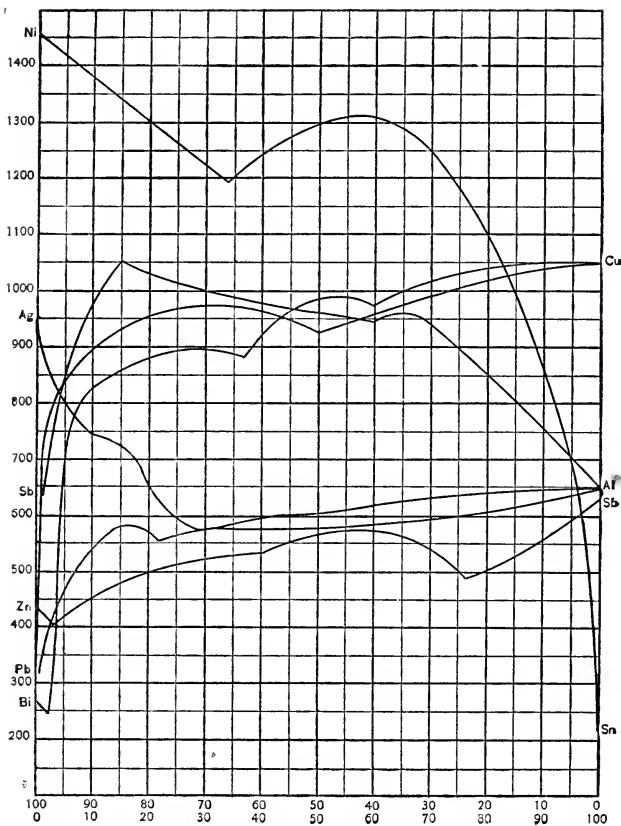
Fig. III.—Diagram showing the melting-points of nickel-tin, silver-aluminium, antimony-copper, zinc-antimony, lead-copper, lead-aluminium, and bismuth-copper alloys. (The ordinates represent degrees C. ; the abscissae, percentages of the two constituents of each alloy.)

solution is secured and the copper is refined, has been described by Whitehead,[1] and the separation and preparation of pure tellurium has also been recently described.[2] It will suf-

[1] J. Am. Chem. Soc., **17**, 280, 848.
[2] This JOURNAL, **23**, 105.

fice to say here that the method consists in the precipitation
of the metal and its conversion into basic tellurium nitrate,
$Te_2O_3.(OH).NO_3$. This finely crystallized salt serves as an
excellent means of obtaining pure tellurium. The basic ni-
trate is decomposed by heat; the oxide thus obtained is dis-
solved in hydrochloric acid, and from this solution the metal
is reprecipitated by means of sulphur dioxide. Crystallization
of the basic nitrate from a nitric acid solution removes sele-
nium completely from the tellurium, and also furnishes a very
convenient method for the separation of other metals.

Tellurium thus prepared is a black amorphous powder.
After fusion and cooling, however, it is decidedly crystalline,
resembling antimony very markedly in this respect, but in lus-
ter being nearly as bright and white as silver. It is capable of
taking a high polish, but, on account of its brittleness, it is
difficult to get an entirely smooth surface. Its freezing-point
is 446° C., and its specific gravity 6.243.

The Preparation of the Alloys.

Having obtained in this way about 250 grams of pure tel-
lurium, we made 17 alloys, varying in composition from 98
per cent lead and 2 per cent tellurium to 5 of lead and 95 of
tellurium.

The lead used in the experiments was from two different
sources, but both samples were as pure as could be obtained.
The freezing-point of both samples was found to be 322° C.

In mixing the alloys, granulated tellurium was added to
molten lead contained in a porcelain crucible. In every case
it was found necessary to add from 2 to 5 per cent more than
the amount theoretically required, in order to secure the com-
position desired. After the metals had been brought together
the molten mass was thoroughly stirred, and the heat con-
tinued for a few minutes, in order to insure complete fusion.
The mass was allowed to cool in the smoky flame of the
burner. In all cases, when the two metals were brought to-
gether in the crucible, there was an evolution of light and
heat, and the mass solidified to a hard cake, which, in some
cases, was melted only with the aid of the blast-lamp. This
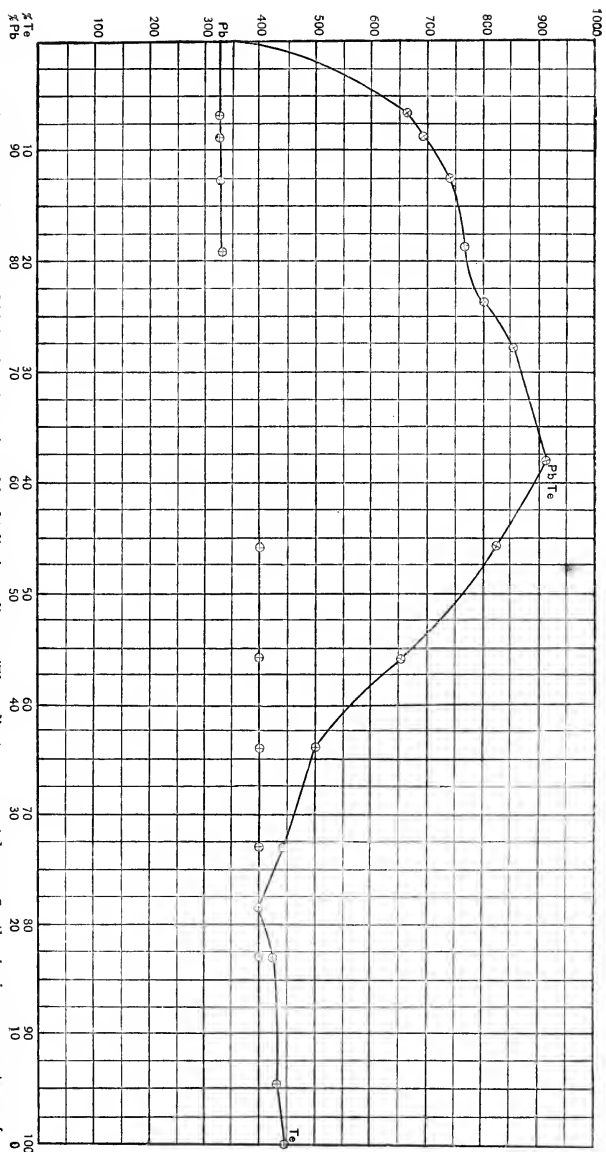hard mass, as will be shown later, was lead telluride.

Fig. IV.—Diagram showing lower and higher freezing-points of lead-tellurium alloys. (The ordinates represent degrees C.; the abscissae, percentages of lead and tellurium, respectively.

Throughout the operation the fused metals were protected from oxidation by a layer of finely-powdered charcoal spread over the surface.

The Analysis of the Alloys.

To obtain samples for analysis, a vertical section one-eighth inch thick was sawed out from the mass of each alloy, one-half being used for analysis and the other half for microscopical examination. As the alloys varied considerably in hardness it was possible to pulverize some of them, while from others the sample was obtained by filing.

No reliable procedure was known for the determination of either lead or tellurium in the presence of the other, and many methods were tried without much success. It was thought that tellurium might be separated by taking advantage of the insolubility of its basic nitrate in strong nitric acid, but concordant results were not obtained. It was also found impossible to remove the lead as sulphate, and to precipitate the tellurium from the sulphuric acid filtrate.

The method finally employed for the analysis of all of the alloys consisted in volatilizing the tellurium as chloride, in a current of chlorine gas, and weighing the residue of lead chloride. It was found that by keeping the temperature near the fusing-point of lead chloride, all of the tellurium chloride could be distilled off without loss of lead. This method was found to be very convenient, accurate, and rapid. Table I., showing the tabulated results of the analyses, gives the percentage of lead as found by analysis, and that of tellurium as calculated by difference.

The Determination of the Freezing-Points.

All determinations of freezing-points were made with a Le Chatelier thermo-electric pyrometer. The electric couple of this pyrometer consisted of a pure platinum wire and a wire of platinum alloyed with 10 per cent of rhodium. These wires were soldered to copper-wire leads, connecting them with a galvanometer of the d'Arsonval type, which reflected a beam of light upon a millimeter scale. The junction was calibrated by noting the deflections corresponding to the following known points, stated in centigrade degrees :

	Boiling-points.		Freezing-points.
Water	100	Aluminium	660
Naphthalene	218	Gold	1072
Sulphur	445	Copper	1095

The deflections were such that by reading to tenths of a millimeter one could estimate the temperature within 2° C.

Since both lead and tellurium alloyed very readily with either platinum or platinum-rhodium, it was found necessary to protect the junction. This was satisfactorily effected by threading the wire through a piece of hard-glass tubing of small diameter, bent into a long, narrow ∪.

In determining the freezing-point of an alloy, the junction was placed in a molten mass, contained in a porcelain crucible, and readings were made every ten seconds during the cooling. In this way the freezing-points given in Table I., and shown graphically in Fig. IV., were determined.

The Microscopical Examination of the Alloys.

Each sample for microscopical examination was one-half of the vertical cross-section, one-eighth inch thick, which had been sawed from the center of the mass of each alloy, the other half of the section having been used for analysis. The surface was first smoothed with a file, and then by rubbing under

Table I.—Freezing-Points and Percentage Composition of Lead-Tellurium Alloys.

(Shown graphically in Fig. IV.)

Alloy. No.	Lead. Per cent.	Tellurium. Per cent.	Lower freezing-point. Deg. C.	Higher freezing-point. Deg. C.
1	100.00	....	...	322
2	94.00	6.00	320	665
3	91.30	8.70	325	695
4	87.50	12.50	322	743
5	81.40	18.60	322	775
6	76.40	23.60	...	805
7	72.20	27.80	...	859
8	61.97	38.03	917	917
9	54.10	45.90	397	828
10	43.70	56.30	400	656
11	35.90	64.10	400	550
12	27.20	72.80	400	445
13	21.50	78.50	400	400
14	17.00	83.00	400	427
15	5.60	94.40	...	433
16	....	100.00	446	446

Fay and Gillson.

water on an Arkansas stone. The final polish was accomplished by rubbing very lightly on rouge placed on chamois. The surfaces were all etched with very dilute hot nitric acid, which brought out the structure satisfactorily. The alloys containing not more than 38 per cent of tellurium could be
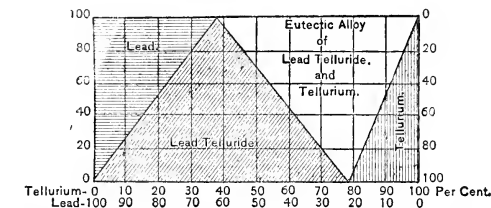

Fig. V.—Diagram showing the percentage of each constituent in various lead-tellurium alloys.

etched by polishing in relief, but the process was laborious and had no particular advantage over etching with nitric acid.

All the photographs from which Figs. VI. to XII. have been made, were taken at 95 diameters' magnification, and have been reproduced by the engraver at 80 diameters.

Discussion of Results.

Upon inspection of the freezing-points given in Table I., and shown graphically in Fig. IV., it is seen that the freezing-point of pure lead is raised to a remarkable extent by the addition of small amounts of tellurium. For example, in alloy No. 2 the addition of 6 per cent of tellurium has caused a rise in the freezing-point of over 300° C., but the further addition of tellurium has not caused a proportionate elevation of the freezing-point. The maximum freezing-point, 917° C., was reached when the composition of the alloy corresponded to that of lead telluride, PbTe. The formation of lead telluride explains the evolution of light and heat, and the rapid rise in the freezing-point caused by bringing together the two metals. The metallic lead very easily becomes supersaturated with the lead telluride, and the latter separates out of the solution. As the cooling is carried further, the excess of lead separates. This separation of the two constituents is well shown in the freezing-points of alloys Nos. 3, 4, and 5. The lead point,
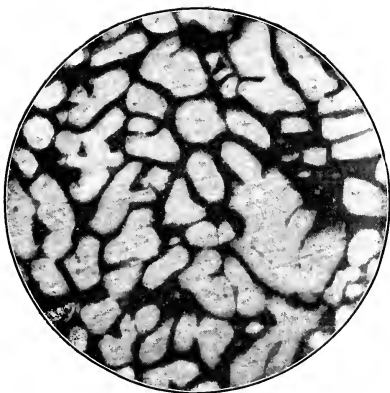
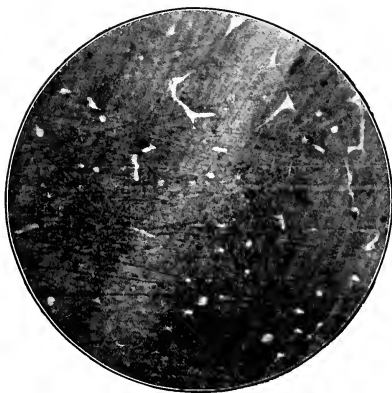Fig. VI.—Alloy No 4. Lead and lead telluride.
(80 Diameters.)

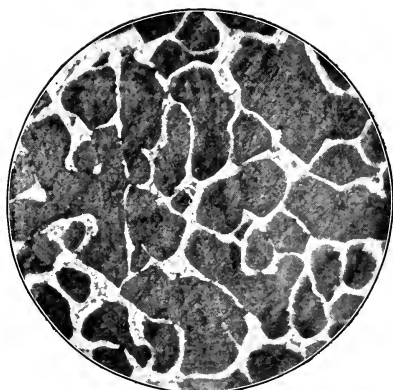Fig. VII.—Alloy No. 8. Lead telluride.
(80 Diameters.)

Fig. VIII.—Alloy No. 9.   Lead telluride and eutectic.
(80 Diameters.)

Fig. IX.—Alloy No. 10.   Lead telluride and eutectic.
(80 Diameters.)

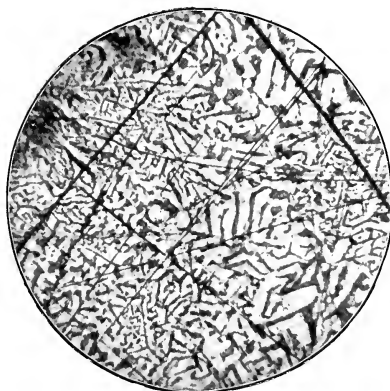Fig. X.—Alloy No. 11.   Lead telluride and eutectic.
(80 Diameters.)

Fig. XI.—Alloy No. 13.   Pure eutectic.
(80 Diameters.)

Fig. XII.—Eutectic and tellurium.
(80 Diameters.)

however, disappears or becomes so weak as not to be noticeable, when the tellurium is in excess of 20 per cent. With an increase of tellurium beyond 38 per cent, the freezing-points are lowered, and the fall continues until a temperature of 400° C. is reached.

At this point the alloy solidifies as a whole, and contains 78.50 per cent of tellurium. This alloy is the eutectic of lead telluride and tellurium. The four alloys, Nos. 9, 10, 11, and 12, all showed two points of solidification, corresponding to the separation of lead telluride and the eutectic alloy. The eutectic was prepared in pure condition by allowing alloy No. 11 to solidify partially, and then pouring off the portion remaining liquid. An alloy prepared in this way gives a constant melting-point of 400° C., and shows under the microscope the characteristic eutectic structure shown in Fig. XI.

With increase in the amount of tellurium beyond the eutectic point, the freezing-point gradually rises to that of pure tellurium, 446° C. The freezing-point of tellurium is variously given from 452° to 525° C., but 446° C. has been repeatedly determined on samples, the purity of which was almost beyond question, since, by reason of the method of their preparation, they could not have contained more than mere traces of impurities.

The Microstructure of the Alloys.

The structure of the alloys strongly confirms the curve of fusibility. In Fig. V., constructed from data obtained from the fusibility curve, the composition of any alloy can be seen at a glance. In Fig. IV. it will be seen that the branch of the curve which connects the melting-points of pure lead and lead telluride represents a mixture of lead and lead telluride. The branch connecting the melting-point of lead telluride and the eutectic represents a mixture of these two constituents; the branch from the eutectic point to pure tellurium, a mixture of tellurium and the eutectic alloy. From Fig. V., the percentage-composition of each constituent can be ascertained. For instance, alloy No. 4, melting at 743° C., contains 32 per cent of lead telluride and 68 per cent of lead. This is shown well in Fig VI., where the light constituent is lead and the

dark is lead telluride. With 38 per cent of tellurium, the
whole mass should consist of lead telluride, and this is shown
in Fig. VII., from a photograph of alloy No. 8. The effect of
an increase in the amount of tellurium we find in alloy No. 9
(80 per cent of lead telluride and 20 of the eutectic). This is
nicely shown in Fig. VIII., where a small amount of the
eutectic has made its appearance between the large granules
of lead telluride. Fig. IX. represents a photograph from
alloy No. 10, containing 46 per cent of eutectic and 54 of lead
telluride. The latter is shown as dark crystallites embedded
in the eutectic. Alloy No. 11 consists of 68 per cent of eutec-
tic and 32 per cent of lead telluride. A mixture of these two
substances in this proportion is shown in Fig. X. Fig. XI.
shows a photograph taken from the pure eutectic, made by
allowing about two-thirds of one of the alloys to solidify, and
then pouring off the still liquid mass. A mixture of the eutec-
tic and an excess of tellurium is shown in Fig. XII. The
photographs do not represent exactly the percentages of each
constituent, but only approximately. On account of the lead
telluride being much lighter than lead, a marked segregation
was found in the alloys composed of these two constituents.
Lead telluride and the eutectic have nearly the same specific
gravity, and consequently show a more homogeneous struc-
ture.

It will be seen from the photographs, and from the diagram,
Fig. V., that lead telluride is a constituent common to all of
the alloys. Its amount gradually increases, as tellurium is
added to lead, until the whole mass is lead telluride, and then
it gradually decreases until the whole mass is pure tellurium.
Tellurium forms a eutectic alloy with lead telluride, but the
latter does not form a eutectic alloy with lead. The form of
the curve seems to indicate an isomorphous mixture between
lead and lead telluride, and the microstructure of the alloys
very low in tellurium seem to point in the same direction.
But the two constituents differ so widely in fusibility that
there is no definite means of knowing whether or not they are
really isomorphous. The isomorphism of these two sub-
stances seems all the more probable when we take into con-
sideration the fact that the mineral, altaite, $PbTe$, crystallizes

in the isometric system, and it is well known that lead crystallizes in that system.

The hardness of the alloys increases with the amount of tellurium present. The alloys containing over 50 per cent of tellurium are very brittle.

It is proposed to continue this study with other tellurium alloys.

XXXVI.—THE ALLOYS OF ANTIMONY AND TELLURIUM.

By Henry Fay and Harrison Everett Ashley.

The study of an entirely new series of alloys may be undertaken from a desire to obtain knowledge applicable to the perfection of industrial alloys, or merely to test certain theoretical considerations. In the case of antimony-tellurium alloys, the theoretical side only is at present important, but it is hoped that the results of this investigation may have some industrial value, at least indirectly, by furnishing one more example for comparison when studying commercial alloys.

The statement is found in various places that antimony is isomorphous with arsenic, bismuth, and tellurium, but very little experimental evidence has been offered in support of this assumption. All four metals crystallize in rhombohedra, and the ratio of the axes $a : c$ is approximately the same—which seems to indicate, but does not prove, their isomorphism. The close association of these metals in minerals also seems to indicate that they are isomorphous. There are, however, certain differences in their properties which render this conclusion somewhat doubtful, and it is therefore desirable that independent evidence be found to decide the question. In a paper on lead-tellurium alloys[1] it has been shown that two metals which are isomorphous give, as a fusibility-curve, a straight line connecting their melting-points. The best examples of this class of alloys are the alloys of gold and silver, gold and platinum, and bismuth and antimony. In each of these cases the properties of the alloys are a mean between the properties of the two metals. The isomorphism of gold

[1] See preceding article.

and silver and bismuth and antimony might be confirmed by means of the microscope, but, so far as we know, no work has been published on this side of the problem. The microstructure of binary alloys of isomorphous metals should show an intimate mixture of the two metals without any evidence of compounds or of a eutectic mixture. In connection with some work on the isomorphism of selenium and tellurium we had occasion to prepare several bismuth-antimony alloys, in which we found the microstructure to consist of a very homogeneous mixture of the two metals.

It was hoped that by taking advantage of the fusibility-curve which could be established by determining the freezing-points of a series of alloys, and by a study of the microscopical appearance of etched specimens of these alloys, we might be able to form some idea in regard to the isomorphism of tellurium and antimony.

With regard to the more practical side of the problem, it might be said that tellurium and antimony are so similar in their physical properties that the former might replace antimony in some of its alloys. If this should be found possible, it would open up a field of usefulness for the large quantities of tellurium which now go to waste. The effect of even small quantities of antimony on malleable metals, such as copper and gold, is most injurious, making them hard and brittle; but, on the other hand, it gives the necessary hardness to the lead of type metal, and produces valuable alloys with tin in Britannia metal for decorative objects, and, with tin, zinc, and copper, Babbitt metal for bearings. With lead, its 12 per cent alloy, the eutectic mixture of these two metals, possesses valuable properties, and is used on account of its power to resist the action of sulphuric acid for making the so-called "lead chambers" for the manufacture of that acid.

Tellurium likewise possesses the power of hardening other metals. This hardening power is very marked in the alloys with lead, and Roberts-Austen has found that it diminishes the tenacity of gold and copper. So far as we know, no ternary alloys containing tellurium, and corresponding to Britannia or Babbitt metals, have been prepared.

Methods and Apparatus.

In order to study the properties of the tellurium-antimony alloys, sufficient of each metal was taken to form a button weighing about 20 grams. In all, fifteen alloys were made, varying from 5 to 95 per cent of tellurium.

The antimony used was the so-called chemically pure metal, which was found to contain traces of lead and sulphur. Its freezing-point[1] was 624° C., and its specific gravity 6.693.

The tellurium was obtained from the residue of the Baltimore Copper Works, and was purified by the method which was recently given in an article on lead-tellurium alloys. Its freezing-point was 446°, and its specific gravity 6.243.

The mixed metals were put in a porcelain crucible, covered with powdered charcoal, fused over the blast-lamp, and allowed to stand until cold. No heat phenomena were noticed during the melting of the two metals.

From the button thus formed a section was sawed out for microscopic examination, and the larger of the remaining portions was used for a specific gravity determination. The two larger parts were then united and used for the freezing-point determination.

Freezing-temperatures of the alloys were measured by means of a thermo-electric junction in connection with a galvanometer of the d'Arsonval type, made by Keiser and Schmidt, of Berlin, and so arranged that readings could be taken by means of a needle passing over a graduated scale. This type of instrument was found to be not nearly so satisfactory for experimental work as a delicately-adjusted reflecting galvanometer. There was considerable lag in the instrument, which could only be obviated by constant tapping ; and even by this method we were not sure that our results were correct within 5°. The pyrometer was calibrated against the following substances :

	Degrees C.
Boiling water	100
" naphthalene	218
" sulphur	445
Freezing aluminium	660
" gold	1072

[1] This freezing-point does not correspond to the value, 630° C., recently determined by Holborn and Day ; but the slight difference may be explained by the small amount of impurity in our antimony, and by the lag in the galvanometer.

In order to protect the junction from alloying with the vapors of antimony and tellurium, the two wires were passed through two very small hard-glass tubes, and these tubes were then placed in a larger piece of hard-glass tubing of about 5 mm. diameter.

Freezing-Points.

To determine the freezing-points, the alloys were placed in a Battersea annealing cup and were heated to about 100° above their melting-point. The molten mass, protected from oxidation by a layer of finely divided charcoal, was thoroughly stirred to insure complete admixture of the constituents. The junction was placed vertically in the alloy, and readings of the galvanometer were taken every ten seconds, until the temperature had fallen to 100°. The beginning of the various points of retardation was taken as the freezing-point. The results of these determinations are given in Table I., and are shown graphically in Fig. I.

Table I.—Freezing-Points of Antimony-Tellurium Alloys.

Alloy. No.	Antimony. Per cent.	Tellurium. Per cent.	Higher freezing-temp. Deg. C.	Lower freezing-temp. Deg. C.
1	100	0	624	....
2	95	5	623	....
3	90	10	599	....
4	80	20	568	....
5	75	25	547	....
6	70	30	551	....
7	60	40	561	....
8	50	50	599	....
9	38.63	61.37	629	....
10	30	70	613	422
11	20	80	526	419
12	15	85	434	422
13	10	90	421	....
14	5	95	456	....
15	0	100	446	....

It appears from Fig. I., in which ordinates represent temperatures and abscissae percentage-composition, that the antimony-tellurium alloys belong to the class in which occur one or more definite chemical compounds, and in this respect are similar to the lead-tellurium alloys. The compounds in this

class of alloys are always indicated by a maximum point in the fusibility-curve, and by a uniform field when examined under the microscope. In this case it will be seen that the maximum point in the curve corresponds to a freezing-point of 629°, and a composition of 61.37 per cent of tellurium and 38.63 of antimony, which indicates the compound Sb_2Te_3. This compound, antimony telluride, forms a eutectic alloy containing 87 per cent of tellurium, and melting at 421° with tellurium, and is isomorphous with antimony, consequently does not form a eutectic with it. This latter fact places the antimony-tellurium alloys in the sub-class of the third general class of alloys in which one of the compounds is isomorphous with one of the elements. The portion of the curve which connects the freezing-points of antimony and antimony telluride is approximately a straight line, and, considered by itself, represents an isomorphous mixture.

In that part of the curve which is included between 38 and 100 per cent of antimony, we should expect to find, and do find, homogeneous mixed crystals of the pure antimony and antimony telluride. The microscopic field between these two points for all alloys examined is very similar, except where the percentage of antimony is very high, in which case there is some tendency for the telluride to segregate out in masses.

The isomorphism of these two substances seems all the more probable when we consider the fact that the mineral tetradymite, Bi_2Te_3, crystallizes in the rhombohedral system. It is more than likely that the antimony telluride, if it occurred as a mineral, would likewise be found to crystallize in that system. Although tellurium crystallizes in the hexagonal system also, its cleavage indicates that it is not isomorphous with antimony, and consequently not with antimony telluride.

The question might arise as to the existence of a compound of the composition corresponding to the formula SbTe. All we can say at present is that there is no evidence in favor of such a compound. There are no à *priori* reasons why it should not exist, and it is entirely possible that it should exist and form an isomorphous mixture with antimony and antimony telluride, Sb_2Te_3. If it were formed in this mixture we should expect a more marked evolution of heat in the

alloys corresponding to this composition, but the amount of heat evolved in the alloy corresponding to this composition was not above the average for the other alloys.

Oppenheim[1] makes the statement that antimony forms either iron-gray, SbTe, or tin-white, Sb_2Te_3. The only evidence, however, in favor of the compound was that the iron-gray mass was homogeneous and had cleavage planes. The assumption seems to have been based on a very small amount of evidence, for the result of our work shows that with these proportions an alloy is formed which, although brittle, homogeneous, and crystalline, is merely an isomorphous mixture of antimony and antimony tritelluride.

From an inspection of the freezing-point curve it seems to be evident that antimony and tellurium are not isomorphous, as has been generally supposed, and that, consequently, they do not mix at the temperature of fusion as such. On the contrary, tellurium and antimony telluride form a series of alloys which in all respects is similar to the class of alloys of which the lead-tin and silver-copper alloys are good examples. In other words, the freezing-point of either antimony tritelluride or of tellurium is lowered by the presence of the other, no matter which one we consider as the solvent. They are mutually soluble and mix in all proportions.

Percentage Composition of the Constituents.

To express approximately the composition of any particular alloy a diagram, Fig. II., has been constructed, which will show at a glance the percentage of each constituent. The abscissae represent the percentages of antimony and tellurium, and the ordinates the division of the total 100 per cent of the alloy into percentages of tellurium and eutectic alloy, antimony telluride, and eutectic alloy, or isomorphous mixture of antimony and antimony telluride. For instance, an alloy whose chemical composition is 40 per cent tellurium and 60 per cent antimony is made up of a mixture of 35 per cent antimony and 65 per cent antimony telluride. Again, if we wish to obtain an alloy containing 34 per cent of eutectic and 66 per cent of antimony telluride, it is readily seen that it

[1] J. prakt. Chem., **71**, 277.

must consist of 70 per cent of tellurium and 30 per cent of antimony.

Specific Gravities.

In view of the nature of these alloys, it was thought desirable to study the specific gravities, but from the results obtained no conclusion could be drawn. It seems to be true that nearly all the physical properties of alloys are additive and give no clue to the nature of the constitution. Various values for the specific gravity of tellurium have been given. Rammelsberg found for the amorphous variety the value 5.93 and for the crystalline 6.38 to 6.42. At 0°, Spring[1] found for the uncompressed 6.2322, and for the compressed 6.2549. Later, he reported the value 6.22. Klein and Morel[2] found values varying from 6.204 to 6.215, and, recently, Lenher and Morgan[3] have reported the value 6.1993. Priwoznik[4] obtained the value 6.2549 on a specimen which had been carefully prepared, and which had been fused in a current of hydrogen.

Using a specimen of tellurium which had been prepared from recrystallized basic nitrate, we found the value 6.243. This value represents several actual determinations on specimens known to be pure and free from blow-holes, and is also the average of several other determinations on other specimens. The most accurate determination was made from a button weighing from 30 to 40 grams, which had been fused several times under charcoal. This was split in half, and the outside surfaces were smoothed on an emery wheel. It was suspended in boiling water for some time ; the water was allowed to cool, and this button of 18.64 grams was weighed in water and in air. As great care had been taken to remove all traces of silica and selenium, these two substances could not have affected the results. The greatest sources of errors are blow-holes, to which the extreme crystalline character of the metal makes it liable, the inclusion of oxide, and the presence of heavier metals. We have reason to believe that by our method of preparation these factors were avoided.

The specific gravity of antimony telluride is given by

[1] Bull. Acad. Royal Belgique, **5**, 854.
[2] Bull. soc. chim., [2], **43**, 198.
[3] J. Am. Chem. Soc., **22**, 29.
[4] Chem. Centrbl., **2**, 962.

Bödeker and Giesecke as 6.47 to 6.51 at 13°. For the alloy
containing 60 per cent of tellurium we obtained 6.46. The
results for the other alloys were, as a whole, very unsatisfac-
tory, and the values given in the following table are only ap-
proximate. Some of the alloys were so crystalline that it was
impossible to obtain them free from air spaces. In certain
cases large, drusy cavities were found in the center of an in-
got after weighing. This tendency to form intercrystalline
cavities was especially marked in the alloys containing from
o to 40 per cent of tellurium. Beyond this point there was a
tendency for the eutectic alloy to fill up these spaces, as is
shown in Fig. V., where the eutectic has flowed in between
the long, parallel crystals of antimony telluride. The crys-
tals in this case are colored dark on account of superficial
oxidation, but ordinarily are almost silver-white.

*Table II.—Specific Gravities of the Alloys of Antimony and
Tellurium.*

(Shown graphically in Fig. III.)

Weight of specimen. Grams.	Tellurium. Per cent.	Specific gravity.
18.6462	100	6.243
6.1011	90	6.264
0.703	80	[1] 6.56
0.941	80	6.17
3.681	80	6.370
6.201	70	6.370
5.4491	60	6.462
8.9995	50	6.347
3.8007	40	6.496
4.2680	30	6.615
7.7445	25	6.564
6.4322	20	6.601
2.5014	10	6.717
12.3573 (Pure antimony.)	0	6.693

As the percentage of tellurium approaches the amount
necessary for the eutectic alloy, the structure is somewhat
micaceous, some of the planes of fracture showing a matte
surface. This micaceous structure is responsible for a turn-
ing over of edge, and is very evident when one attempts to
pulverize a piece in a mortar. Most of the other alloys show

[1] Three specimens from one ingot.

a remarkable crystalline cleavage, the surfaces of which are very brilliant.

Both antimony and tellurium, and all their alloys, have approximately the same degree of hardness, somewhat above 2.5 (mica) and decidedly lower than 4 (fluorite). From 0 to 20 per cent of tellurium, the alloys closely resemble antimony.

Microscopical Examination of the Alloys.

The preparation of satisfactory samples for microscopic examination proved to be very difficult. On account of the highly crystalline character of some of the specimens, there was a great tendency for small fragments to split out along cleavage planes, thus leaving a pitted surface. By careful treatment a fairly satisfactory surface could be obtained by
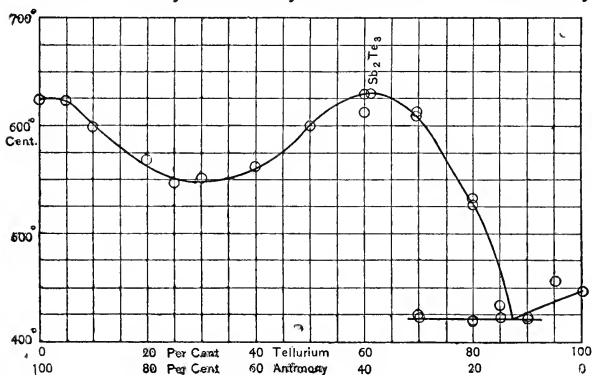
Fig. I.—Freezing-point curve of the alloys of antimony and tellurium.
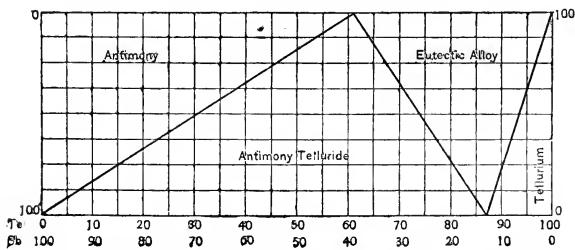
Fig. II.—Diagram showing composition of constituents of the alloys of antimony and tellurium.

first rubbing on an oil-stone under water, then polishing lightly on a wheel with a mixture of rouge and stearic acid, and finally on a piece of chamois stretched on a wooden block.

The process of etching was likewise difficult. Hydrochloric and nitric acids and iodine were all used without any appreciable effect. The best results were finally obtained by electrolysis in either dilute hydrochloric acid or ammonia. The specimen to be etched was attached to one of the poles of a battery and a current of about 0.1 ampere was allowed to pass for a few minutes. The structure was brought out by this means, but there was considerable superficial oxidation which produced beautiful colored effects on the surface. This darkening effect is well shown in Fig. V., where the crystals of Sb_2Te_3 have branched out through the eutectic alloy. Before etching, the whole surface was brilliantly white, but after etching, the crystals were colored a beautiful blue, which, in some cases, revealed the structure to the naked eye. The alloys from 0 to 60 per cent of tellurium were all richly colored, and showed under the microscope a uniform crystalline field with the single exception of the alloy containing 5 per cent of tellurium, which was composed of rounded granules of antimony telluride embedded in pure antimony. A cross section of any of these alloys showed branching crystals extending from the bottom to the top of the ingot.

The alloy containing 61.37 per cent of tellurium presented an absolutely uniform appearance, being composed entirely of the compound Sb_2Te_3, and is shown in Fig. IV. The dark spots in the photograph show the cavities produced as a result of the crystallization. With an increase in the percentage of tellurium beyond this point, the eutectic alloy of antimony telluride and tellurium began to show. In alloy No. 11, Fig. V., this is shown very clearly. In this alloy long crystallites of antimony telluride appear throughout the mass, and the space between the separate crystals is filled with the eutectic. In this case the crystals are dark on account of the superficial oxidation produced in etching.

Fig. VI. shows the appearance of the eutectic alloy, as it was usually found in the alloys containing from 60 to 90 per
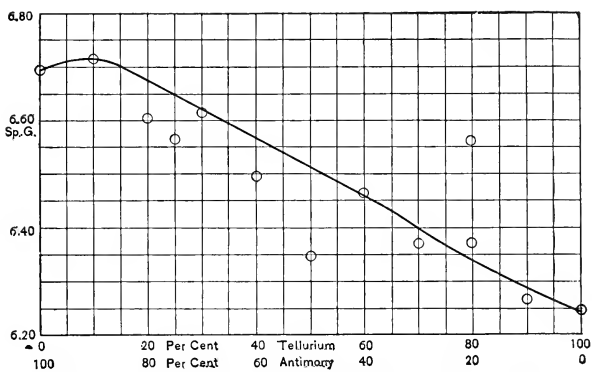
Fig. III.—Specific-gravity curve of the alloys of antimony and tellurium.

Fig. IV.—Alloy No. 9. The entire field consists of antimony telluride, Sb_2Te_3. (Magnified 95 diameters.)

Fig. V.—Alloy No. 11. Dark, crystallites of antimony telluride ; light, eutectic of antimony telluride and tellurium. (Magnified 95 diameters.)

Fig. VI.—Eutectic alloy. Slowly cooled ; etched with hydrochloric acid. (Magnified 95 diameters.)
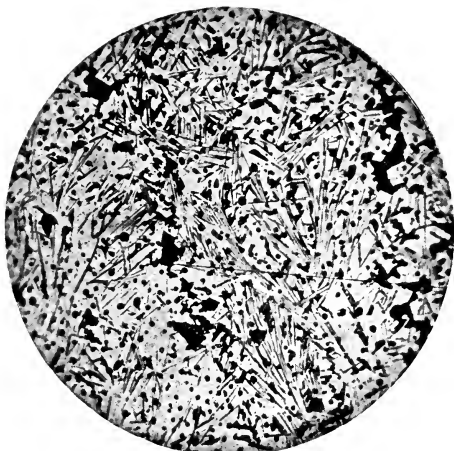
Fig. VII.—Eutectic alloy. Cast on porcelain ; unetched.
(Magnified 95 diameters.)

Fig. VIII.—Alloy No. 15. Light, pure tellurium ; dark, eutectic of
tellurium and antimony telluride. (Magnified 95 diameters.)

cent of tellurium. In slowly cooled alloys the structure was invariably the same, but more rapid cooling produced an entirely different appearance. Fig. VII. represents a photograph of the pure eutectic, prepared from several other alloys by pouring off the still liquid mass after a part had solidified. The photograph represents a surface which had been cast on glazed porcelain, and was taken just as it appeared after cooling, without any further treatment. The light background is tellurium, and the dark portions are antimony telluride. The latter was probably brought out in such great contrast on account of its extreme tendency to oxidize.

Fig. VIII. shows the usual appearance of the alloys consisting of the eutectic and an excess of tellurium.

It is proposed to study in the same manner other binary alloys of tellurium, and subsequently some of the ternary alloys.

XC.—ELECTRO-AFFINITY AS A BASIS FOR THE SYSTEMATIZATION OF INORGANIC COMPOUNDS.

By James Locke.

In an article published a short time ago,[1] Abegg and Bodländer develop the conception "true electro-affinity," which they define as the strength of union between an ion and electron, or the intensity with which an ion holds its charge of positive or negative electricity. They then attempt to show that certain properties and reactions of inorganic salts are directly dependent upon the electro-affinities of the respective negative and positive ions. These properties are, especially, (1) solubility, and the tendency to form complex (2) positive, and (3) negative ions.

(1) *Solubility.*—The authors assert, as a general law, that the greater the electro-affinity of a positive or negative ion, the greater will be the solubility of its salts. The statement is modified, however, by the additional law, that when the electro-affinity of one of the ions is very great, and that of

[1] Ztschr. anorg. Chem., **20**, 453.

the other small, the influence of the first will overcome that of
the second, and the salt of the two will be soluble.   In con-
formity with these laws, salts yielding sodium ions, the elec-
tro-affinity of which is very great, are in almost every case
soluble in water.   Salts yielding silver ions, which have a very
low electro-affinity, are, on the other hand, generally insolu-
ble.   But silver nitrate, inasmuch as the electro-affinity of the
NO_3^- ion is exceptionally high, dissolves readily.   In cases,
however, in which the electro-affinity of both the positive and
negative ions is high, the reverse order seems to be fol-
lowed, and the salts become in such cases less soluble than
when the value for only one of the ions is great.   That this
would necessarily be so is indicated in the fact that for ions of
very small electro-affinity the influence of the latter upon the
solubility increases more rapidly than do the electro-affinities
themselves.   As an approximate measure of the electro-affini-
ties, we may take the decomposition voltage of the salts.
The effect of change in electro-affinity may then be seen in a
comparison of the decomposition voltage values for zinc and
silver.   For silver, in volts, it is —o.78 (H = o), for zinc it
is +o.74.   The increase of 1.52 volts, in passing from silver
to zinc, increases the solubility of the chlorides by the mil-
lion-fold.   The decomposition voltage of sodium is about
+2.8, and at the same rate of progression, therefore, the solu-
bility of sodium chloride would be something like 10,000,000
gram-molecules per liter.   Since work can be gained on the
dissolving of a salt in water, a salt of such solubility would
have too great a supply of energy to be stable at all. The au-
thors assume, therefore, that it passes into a modification with
far less energy, which, accordingly, does not admit of compar-
ison with the zinc and silver salts.   This is an exceedingly
important hypothesis, without which the theory could not
stand for an instant.

   (2) *Formation of Complex Ions.* — Abegg and Bodländer de-
fine a complex compound—metallo-amines, double salts, etc.—
as follows :

   Complex compounds are those in which one of the ionogenic
constituents is made up of a single ion capable of independent

existence (single ion), coupled with an electrically neutral molecule (neutral component).

Thus, potassium ferricyanide has as its ionogenic constituents potassium and the negative complex $Fe(CN)_6^{---}$, which is composed of the single-ion CN^- and the neutral component $Fe(CN)_3$. No distinction is made between compounds which break down into their molecular constituents in solution, such as the salt $KMgCl_3$, and salts, the complex ions of which are stable in solution, *e. g.*, potassium ferrocyanide, $K_4Fe(CN)_6$.

The greater the tendency to ionization, which may be shown by the neutral component, the more loosely, as a natural sequence, will the complex be held together. The greatest tendency to form ionic complexes, therefore, is to be expected in those cases in which the neutral component, if a salt, is one in which both the ionogenic constituents have low electro-affinities. Only very few double salts are known which contain salts of the alkali metals as their neutral components, and such as have been observed (*e. g.*, $KNaCO_3$) are, at least, of extreme instability. On the other hand, the double salts of silver, gold, etc., the electro-affinities of which metals are very low, are plentiful, and marked, in many cases, by the almost total absence of dissociation of their complex ions in solution.

The tendency to the formation of complex ions is also influenced by the nature of the single-ion. Since the product of the electrolysis of complex compounds is almost invariably the single-ion, not the complex, it follows that the electro-affinity of the complex is greater than that of the single-ion. In other words, *the electro-affinity of the single-ion is increased by its union with the neutral component.* Inasmuch, therefore, as in the presence of a strong opposite ion a weak ion is compelled to ionization, it seeks to *strengthen* itself by combination with a neutral component.

This portion of the authors' theory is widely extended to include not only double salts, metallo-amines, hydrated salts, and the like, but also the formation of poly-acids (*e.g.*, $K_2Cr_2O_7 = K_2^+, ^+CrO_4(CrO_3)^{--}$), and even oxy-acids in general. The chlorate ion, ClO_3^-, for instance, is regarded as a complex with a single-ion Cl^- and the neutral component $3O$. To

these extensions of the theory I will return at a later point.

———

The properties of the sodium salts may be briefly summarized as follows :

(1) Solubility in water.

(2) Non-entrance into the negative complexes of double salts.

(3) Non-entrance into complex cations, such as metallo-amines.

(4) Stability on ignition, or passage thereon into another salt, never into the oxide.

These collective properties apply to almost every sodium salt known, and by their application the behavior of each single salt is roughly described. For instance, since sodium does not enter into complex anions, its chloride is less soluble in hydrochloric acid than in water. Potassium salts, like those of sodium, are soluble in water ; and since, in showing this one property, they exhibit in about the same degree all the others common to the sodium compounds, it must be concluded that these properties are not independent of one another, but correlated and due to one and the same ultimate cause. The same is true of the silver and cuprous compounds. In so far as they are capable of existence, the cuprous compounds, in exhibiting a single generic property common to silver compounds, conform to the latter in all their generic reactions, exclusive of those of oxidation.

Any theory which brings to the front a cause to which these properties may be due, must be of the greatest service to the science. This the theory of Abegg and Bodländer in part attempts, for it refers each of the properties enumerated, indirectly that of stability on ignition as well as the others, to the approximately equal values of the electro-affinities of the metals in the sodium group and silver group respectively. But as a direct sequence of the theory these properties should always go hand in hand with one another. Exceptions in regard to the solubilities of a few individual salts can be explained as the authors have explained the relative solubility of sodium chloride and zinc chloride. But any instance in which one generic property of, let us say, silver salts is shown

in extenso by the compounds of a metal, when they have not the remaining generic properties of silver salts, must be regarded only as a flat contradiction of the theory, and render its admissibility at least very doubtful. This is especially true in a case in which the electro-affinity of the metal approximates that of silver.

The electro-affinity of thallous thallium is very small, and this fact is used by the authors to explain the slight solubility of thallous halides. In addition to the iodide, the sulphide, chromate, dichromate, sulphocyanate, vanadate, hypophosphate, ferrocyanide, and other compounds are practically insoluble in water. These are also the most difficultly soluble silver salts. The sulphite, thiosulphate, triorthophosphate, chloride, bromide, and many others, dissolve only slightly. The solubility, in general, is somewhat greater than that of silver salts, but less than that of zinc and cadmium compounds; and thallium, in accordance herewith, has a much lower electro-affinity than have these metals. Now both zinc and cadmium yield double salts in which they form part of the neutral components. They form metallo-amines—complex positive ions—in great plenty and of much stability. How much more readily, therefore, should such salts be formed by thallium, which, in the matter of electro-affinity, is nearer silver, and which, like the latter metals, forms sparingly soluble salts. Not a single metallo-amine of thallous thallium has ever been prepared. Thallous chloride is far less soluble in chloride solutions,[1] the iodide in iodide solutions, than in water. Were it not for a complex thiosulphate and sulphocyanate, we might justly say that the power of thallium to enter into double salts is absolutely *nil*. A double salt of thallium with one of the weakest anions, S^{--}, cannot be obtained even in the dry way.

We have here, therefore, two of the three generic properties of salts of a metal with low electro-affinity almost entirely absent—the formation of complex cations and complex anions—while the third, sparing solubility, is present in full force. Nor is this the only refractory case. There are almost as many others as there are elements, and one or two of these I may

[1] Noyes : Ztschr. phys. Chem., 9, 606.

touch upon briefly. It will be seen that while the salts of metals of the same valence can almost always be divided into groups according to their generic properties, as above, we do not necessarily find the same properties in correlation. A tendency to double salt formation does not in the least necessitate a tendency to form complex cations ; nor does general slight solubility in water necessitate the formation of either anions or cations of complex nature.[1]

Dividing the metals into groups according to their valence, the authors state that their electro-affinities lie, in general, in the same order as the positions of the elements in the periodic system. In the different families the electro-affinities increase with increasing atomic weight. The series Cu^I, Ag, Au^I, and Zn, Cd, Hg^{II}, follow the reverse order. While " direct measurements are in most cases wanting, this arrangement is obvious from the solubilities, strength of acids, and general chemical behavior." As has been stated, the electro-affinities may be roughly measured by the decomposition voltage of the metals. To show the relative magnitudes I include some of these values in the following table :

Li	Be	N	F
Na($+2.8$?)	Mg($+1.47$)	P	Cl($+1.31$)
K	Ca	As	Br($+0.94$)
Rb	Sr	Sb(-0.13)	I($+0.52$)
Cs	Ba		

	Au		Hg
	Ag(-0.78)		Cd($+0.38$)
	Cu		Zn

Furthermore, for members of the eighth family, we have :

$$Mn(+1.06) \qquad Fe^{II} +0.33 \qquad Ni +0.22 \qquad Co +0.22$$
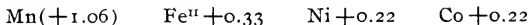
The decomposition voltage of the alkaline earth metals has not been determined, but it is undoubtedly higher than that of magnesium, and less than that of sodium.

[1] That the electro-affinity theory requires this correlation, nevertheless, is shown by Abegg and Bodländer themselves. The instance of platinic platinum is cited as an exception in that while yielding double salts in abundance it forms metallo-amines with difficulty. They explain this by the assumption that the platinic ion is so weak that it can hardly exist even when strengthened by the addition of NH_3 molecules. This difficulty, however, may easily be overcome by considering only cases in which the metallic ions are easily capable of independent existence—*e. g.*, Ba+ +, Zn+ +, etc.

Now let us compare the solubilities of the barium salts with those of sodium on the one extreme and of zinc on the other. The statement of Abegg and Bodländer, that when both cation and anion possess very great electro-affinities the salt is apt to pass into a form unsuitable for comparison, should apply to barium salts in a less degree than to those of sodium, since the electro-affinity of barium is less than that of sodium. But to avoid confusion arising from this source, the following list has been made up mainly of salts of weak anions:

	Sodium.	Barium.	Zinc.
Nitrate	Sol.	>Sol.<	Sol.
Chloride	"	>Sol.<	"
Fluoride	"	Insol.	Slightly sol.
Sulphate	"	"	Sol.
Chromate	"	"	"
Selenate	"	"	"
Thiosulphate	"	>Slightly sol.<	"
Hypophosphite	"	>Insol.	"
Iodate	"	"	"
Phosphite	"	"	"
Silicofluoride	"	"	"
Sulphite	"	>Slightly sol.<	"
Dithionate	"	>Sol.<	"
Nitrite	"	"	"
Hyponitrile	"	Insol.	..
Oxalate	"	"	Sol.
Carbonate	"	"	Insol.
Phosphate	"	"	"
Cyanide	"	Slightly sol.	"

Among the salts of other acids there are a few, such as the arsenates, of which both the barium and zinc salts are insoluble; in the majority of cases, however, no data can be obtained for comparison. But from this list alone it can readily be seen that the barium salts are, in general, insoluble or sparingly soluble, that the corresponding zinc salts are usually soluble. As a rule, furthermore, the solubilities of the calcium salts approximate those of barium, though somewhat higher (in spite of the fact that the electro-affinity of calcium is less). But neither of these metals, though their salts are sparingly soluble, show in more than the slightest extent a tendency to enter into complex ions. The only double salt of barium with a monobasic acid, mentioned in Dammer, is

the compound $K_2Ba(NO_2)_4$. Ammonia addition-products can be obtained only in the dry way, and these break down completely into salt and ammonia in presence of water.

The solubilities of the salts of magnesium, manganese, ferrous iron, nickel, cobalt, copper, and cadmium are qualitatively almost exactly the same as those of zinc compounds, though in the matter of decomposition voltage the metals range from $+ 1.47$ to $+ 0.22$. Here, in the matter of solubility, we have quantitative data which can be compared directly with the electro-affinities, or with the decomposition voltage values, which roughly measure the latter. The solubilities of the nitrates, $M(NO_3)_2.6H_2O$, at 18°, expressed in gram-molecules per liter of solvent, are as follows :[1]

	Mg.	Mn.	Fe.	Co.	Ni.	Cu.	Zn.	Cd.
Solubilities	4.95	7.41	4.57	5.40	5.12	6.13	6.08	5.37
Voltage	+1.47	+1.06	+0.33	+0.22	+0.22	—0.34	+0.74	+0.38

There can be no question here as to whether a relation exists between solubility and decomposition voltage. Magnesium nitrate, instead of being the most soluble, is, with one exception, the least so. Cupric nitrate is the most soluble, with one exception, and copper has by far the lowest decomposition voltage and electro-affinity.

I have determined the solubilities of the isomorphous double sulphates of the formula $M_2^IM^{II}(SO_4)_2.6H_2O$ with similar contradictory results. Not only is the order different from that of the decomposition voltage values, but from that of the nitrate solubilities as well. For the ammonium salts, at 25°, the solubilities are as follows :

Mg.	Mn.	Fe.	Ni.	Co.	Cu.	Zn.	Cd.
0.791	1.321	....	0.261	0.500	0.778	0.480	2.125
+1.47	+1.06	+0.33	+0.22	+0.22	—0.34	+0.74	+0.38

For the discussion of these figures, suffice it to point out that the solubility of the nickel salt is one-third that of the magnesium compound, while the difference between the decomposition voltages of the two metals is about the same as that which causes the difference in solubility of zinc chloride

[1] Funk : Ztschr. anorg. Chem., **20**, 393, f.f.

and silver chloride (see above, where the statements are a more or less literal translation of the author's words) ; and that although the copper salt, by analogy, should be about as soluble as silver chloride, it too is three times as soluble as the nickel salt.

In spite of the fact that the salts of these metals are, in general, more soluble in water than those of the alkaline earths, and the latter enter into no complex ions, we have in this group stable or unstable complex ions of either positive or negative nature. The double cyanides of all except magnesium are in fact very stable indeed. Double chlorides, bromides, iodides, exist in great abundance. Stable complex amines are known of all the heavier metals of the group, and in concentrated ammoniacal solution magnesium probably forms them to a marked extent as well.[1] These metallo-amines, however, show, like the double salts, no gradation in accordance with electro-affinities, a fact observed and commented upon by Dawson and McCrae.[2] These investigators found from measurements of distribution constants on ammoniacal solutions containing salts of nickel, copper, zinc, and cadmium, that the tendency to form complex ions is about the same for all, although the decomposition voltage of the metals ranges from $+0.22$ to $+0.74$.

The thallous salts, as has been seen, show the sparing solubility which is in conformity with the low electro-affinity of thallium, while in other respects they approach the salts of the alkali metals, and have properties exactly the reverse of those which we would expect. The zinc salts, on the other hand, although the electro-affinity of zinc is likewise low, are mostly very soluble ; but then they conform to its magnitude in yielding both positive and negative complex ions. To touch briefly upon the trivalent metals, the salts of aluminium and iron with weak acids, so far as they have been obtained, are, as a rule, insoluble bodies. They also form double salts with readiness, in conformity with the low electro-affinities of the metals. But no positive complex ions of these metals are known. Ammonia simply precipitates the

[1] Unpublished experiments of the author.
[2] Ztschr. anorg. Chem., 26, 99.

8-27

hydroxides. There may be a few cases in which the three properties called for by the theory go hand in hand, and these Abegg and Bodländer have sought out and used with great dexterity. But inorganic chemistry is not the chemistry of sodium and silver alone.

Double Salt Formation.—For the purpose of discussion, we may divide double salts into three classes :[1]

A. Salts, the complex ions of which are not appreciably decomposed in solution.

B. Salts, the negative ions of which dissociate to a very marked extent, but which are obtained by crystallization from solutions containing equivalent quantities of their molecular constituents.

C. Salts almost completely dissociated, like the last, but which form only when one of their constituents is present in excess.

According to the view of Abegg and Bodländer, the weaker the anion of a double salt is, the more readily will it seek to *strengthen itself by the addition of a neutral component.* Referring for the moment only to the double salts, the single ions of which are univalent, we see that in the compounds of class *A* this seems to be true. The most frequent double salts of this class are the complex cyanides, the neutral components of which are insoluble in water. This latter fact is in accord with that part of their theory which states that *the stronger the anion is the more soluble will be the salt.* But the authors seem to have absolutely lost sight of this feature of their theory in its application to the unstable double salts of class *B*, the existence of every member of which is in direct contradiction to it. If the anion of a chloride is strengthened by the addition to it of a neutral chloride, then the resulting double salt should be more soluble than the simple chloride itself. Professor H. L. Wells, and his co-workers in this laboratory, have found, in long investigations of double caesium halides, that hardly a single such salt, if any at all, is more soluble than caesium chloride alone. I have found that in the case of the alums,[2] where the electro-affinity of the

[1] Wells : This JOURNAL, **26,** 389.
[2] *Ibid.*, **26,** 166.

SO_4^{--} ion is strengthened by the addition of the neutral component $M_2^{II}(SO_4)_3$, (A and B, p. 472 f.f.), the fall in solubility from the potassium to the rubidium, and finally to the caesium, salts is enormous. In gram-molecules per liter the solubilities of the chromium alums at 25° are as follows:

K	0.441
NH$_4$	0.407
Tl	0.212
Rb	0.078
Cs	0.015

Two objections may be offered to this from the standpoint of the theory. First, in that when cation and anion are very strong, the salt will tend to be more sparingly soluble. Secondly, in that, as Abegg and Bodländer state, solubility at a definite temperature does not necessarily afford a suitable means of comparison. In answer to the first, we find that hardly a single simple potassium salt exists, which is more soluble than the corresponding caesium salt—in other words, that the fact of potassium salts being less soluble than those of sodium (owing to the greater electro-affinity of potassium over that of sodium, the salts of which show decreased solubility (A and B, p. 462), is absolutely no proof of this hypothesis. For caesium has, according to their own words, a higher electro-affinity than potassium. As regards the comparison at a given temperature, secondly, the justness of this comparison is proved by the fact that at the same temperature the solubilities of all the alums stand in definite mathematical relation to one another.[1]

A simple application of the law of solubility products will show at once not only that the solubility of an unstable double salt of class *B* must necessarily be less than that of its constituents, but that the absolute solubility of such compounds is in reality very small indeed. It has been shown again and again that in the equilibrium equation of a solution containing potassium sulphate and aluminium sulphate,

$$a_{K_2SO_4} \ b_{Al_2(SO_4)_3} = K \ c_{K_2Al_2(SO_3)_4}.$$
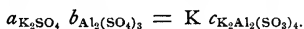
The dissociation constant K is very large. The high value

[1] This JOURNAL, **26**, 332.

of the solubility-product is, therefore, due entirely to this fact, and the solubility of the undissociated alum correspondingly small.

The same conclusion must be reached if we regard the double salt as resulting from the preliminary formation of its complex ions ; for the concentration of the latter, and therefore the solubility-product as well, must have, at least, an extremely low value.

But while the caesium double salts are probably in every case less soluble in water than the simple caesium salts, in contradiction to the theory, the relative solubilities of double salts of this metal, as compared with isomorphous compounds of the remaining alkali metals and ammonium and thallium, show no strict regularities. In the case of the double halides, it has generally been found that the solubilities decrease from potassium to caesium. But with double sulphates no definite order is retained throughout different salt series. This is illustrated, for instance, in a comparison of the alums and double sulphates of the type $M_2^1Ni(SO_4)_2.6H_2O$ at $25°$.

$M^1Cr(SO_4)_2.12H_2O$.		$M_2^1Ni(SO_4)_2.6H_2O$.	
K	0.441	Cs	0.495
NH_4	0.407	NH_4	0.261
Tl	0.212	K	0.210
Rb	0.078	Rb	0.143
Cs	0.015	Tl	0.070

There can be no thought here of a conformity to any one of the laws proposed by Abegg and Bodländer. The relatively great solubility of the thallium alums, in spite of the low electro-affinity of thallium, is opposed to them in the one instance ; and in the other absolutely no suggestion of gradation according to the theory can be found.

The further extension of the theory is so indefinite and faulty that one can hardly tell where to begin, still more where to leave off, in criticizing it. The authors go beyond the definition of complex compounds cited above, in including among these the acid salts on the one hand and basic salts on the other. In these cases the neutral components are replaced by the ionogenic components, H^+ and $(OH)^-$. As an instance of the strengthened nature of the resulting com-

plex ion, the increase in solubility of acid salts over neutral salt is cited ; *e. g.*, barium acid sulphate, barium acid phosphate, barium acid carbonate, etc. The metallic ions, in analogy, must be *strengthened* by the addition of hydroxyl groups. Are basic salts, then, more soluble than the normal compounds? It is difficult to understand how any one who has ever partially neutralized a copper nitrate solution, or who has even ever seen a reasonably old solution of ferric chloride, can make such an assumption.

A great many compounds are cited, with reference to one property or another, by Abegg and Bodländer. At least as many as one-half their examples, if observed with reference to any other properties than those chosen, would be flatly contradictory to their views. For instance, the chlorate ion, ClO_3^-, is the chlorine ion, Cl^-, strengthened by oxygen as a neutral component. Many chlorates are, therefore, more soluble than the chlorides. The periodate ion is the iodine ion strengthened in the same manner. Periodates must, therefore, be more soluble than iodides ! The very weak ion Hg^{++} strengthens itself by the addition of another Hg, thus forming the much stronger mercurous ion $(Hg.Hg)^{++}$. Are then the mercurous salts more soluble than the mercuric ?

The physical chemist is not the only one who regrets the more or less tardy acceptance of the newer theories by the teachers of inorganic subjects. There are many of us whose line of study lies wholly in inorganic fields, who are willing and anxious to do such missionary work as we can for the extension of those theories. But the publication of such speculations as the above, by men prominent in the physicochemical world, does not materially assist toward that end, for it naturally raises doubts as to the accuracy and range of our colleagues' knowledge of practical chemistry. It is as a protest in the name of that practical, experimental chemistry, that the above criticisms are submitted.

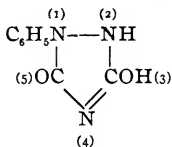# CONSTITUTION OF PHENYLURAZOLE (I.)

BY S. F. ACREE.

Phenylurazole was first made by Pinner,[1] and several derivatives have been described since then, but the constitution of none of these compounds has been determined. Various formulas have been suggested for phenylurazole itself, and it must have one of the following:

$$
\begin{array}{ccc}
\underset{\text{I.}}{
\begin{array}{c}
C_6H_5N\text{---}N \\
| \quad\quad || \\
HOC \quad COH \\
\diagdown \diagup \\
N
\end{array}}
&
\underset{\text{II.}}{
\begin{array}{c}
C_6H_5N\text{---}N \\
| \quad\quad || \\
OC \quad COH \\
\diagdown \diagup \\
NH
\end{array}}
&
\underset{\text{III.}}{
\begin{array}{c}
C_6H_5N\text{---}NH \\
| \quad\quad | \\
HOC \quad CO \\
\diagdown \diagup \\
N
\end{array}}
\end{array}
$$

$$
\begin{array}{cc}
\underset{\text{IV.}}{
\begin{array}{c}
C_6H_5N\text{---}NH \\
| \quad\quad | \\
OC \quad CO \\
\diagdown \diagup \\
NH
\end{array}}
&
\underset{\text{V.}}{
\begin{array}{c}
{}^{(1)}\quad {}^{(2)} \\
C_6H_5N\text{---}NH \\
| \quad\quad | \\
{}_{(5)}OC \quad COH_{(3)} \\
\diagdown \diagup \\
N \\
{}_{(4)}
\end{array}}
\end{array}
$$
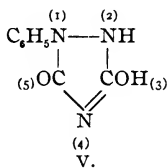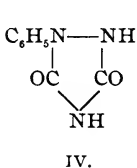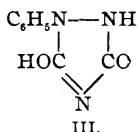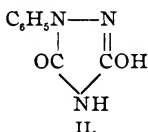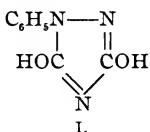
It will be shown that formula V. is the only one that harmonizes with the results obtained.

In designating the position of the groups attached to the urazole ring we shall make use of the system now in vogue, numbering the five atoms in the ring, as follows:

$$
\begin{array}{c}
{}^{(1)}\quad\quad {}^{(2)} \\
C_6H_5N\text{--}\text{--}NH \\
| \quad\quad\quad | \\
{}_{(5)}OC \quad\quad COH_{(3)} \\
\diagdown \diagup \\
N \\
{}_{(4)}
\end{array}
$$

A substance with this formula has the name 1-phenyl-2-hydro-3-hydroxy-5-oxyurazole. A substance with the formula

[1] Pinner: Ber. d. chem. Ges., **20**, 2360; **21**, 1220.

$$C_6H_5N\text{——}NCH_3$$
$$OC \quad CO(COCH_3)$$
$$N$$
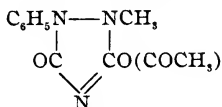
has the name 1-phenyl-2-methyl-3-oxyacetylurazole.

It was shown by Bailey and Acree[1] that triazole derivatives of propionic acid,

$$HOC\overset{N\text{—}N\text{—}CH(CH_3)COOH}{\underset{N=CR}{\Big\langle}},$$
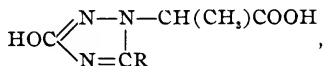
are strong dibasic acids giving a sharp reaction with two molecules of sodium hydrate, using phenolphthaleïn as the indicator, that is, the triazole group,

$$-NHCO-\ \rightleftharpoons\ -N=C(OH)-,$$

is a strongly acid group forming neutral sodium and silver salts, $-N=C(OM)-$. If phenylurazole had the formula I., II., or III., it should form a neutral disodium (or disilver) salt with the formula

$$C_6H_5N\text{——}N$$
$$MOC \quad COM.$$
$$N$$
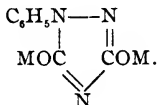
But phenylurazole is a monobasic acid, giving a sharp reaction with one molecule of sodium hydrate and giving only a monosilver salt. Although the disodium salt can be formed by boiling phenylurazole with sodium alcoholate, in absolute alcohol, yet it gives a strongly alkaline reaction when dissolved in water, indicating that one of the sodium atoms of the salt is joined to a nitrogen atom of the urazole ring.[2] Phenylurazole must then have the formula IV. or V. Since it gives a violet color with ferric chloride in alcohol solution just as phenol, acetoacetic ether, and triazoles[3] do, it is very likely that the substance has an enol group, $-N=COH-$.

[1] Bailey and Acree : Ber. d. chem. Ges., **33,** 1520.
[2] Thiele and Schleussner : Ann. Chem. (Liebig). **295,** 171.
[3] Bailey and Acree : Ber. d. chem. Ges., **33,** 1520.

Hence formula IV. is excluded, and phenylurazole has the formula V.,

$$C_6H_5N—NH$$
$$OC \quad COH,$$
$$N$$
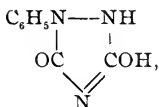
or is 1-phenyl-2-hydro-3-hydroxy-5-oxurazole.

The silver salt, beyond question, has the formula

$$C_6H_5N—NH$$
$$OC \quad COAg.$$
$$N$$
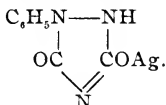
When treated with ethyl iodide in absolute ether in the cold, it gives the 1-phenyl-2-hydro-3-ethoxy-5-oxurazole,

$$C_6H_5N—NH$$
$$OC \quad COC_2H_5,$$
$$N$$
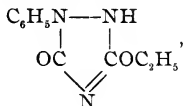
insoluble in alkalies. The imide $=NH$ group of a urazole or triazole ring is not acid enough, or does not give enough hydrogen ions, to form neutral salts in a water solution. The neutral salts of these urazoles have the metal combined with oxygen, forming the group $—N=C(OM)—$, and only when we have an imide group next to a carbonyl group as

$$—NH—CO— \quad \rightleftharpoons \quad —N=C(OH)—$$
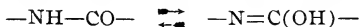
can we have these neutral salts formed. Wheeler[1] has made the isomeric compound with the ethoxy group at 3, and it is soluble in alkalies, as we should expect, forming the salts

$$C_6H_5N—N$$
$$MOC \quad COC_2H_5,$$
$$N$$
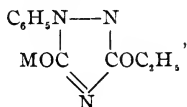
and is precipitated by strong acids. When the isomeric

[1] Wheeler: J. Am. Chem. Soc., 1900, p. 377.

5-ethoxy compound is made it will doubtless have acid properties, forming the salts

$$
\begin{array}{c}
\mathrm{C_6H_5N\!-\!\!-\!N} \\
| \quad\quad || \\
\mathrm{C_2H_5O\!-\!C \quad COM.} \\
\diagdown\diagup \\
\mathrm{N}
\end{array}
$$
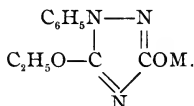
When the sodium or silver salt of phenylurazole is treated with methyl iodide in alcohol at 100° C. a N-methyl derivative having the melting-point 183° to 185° is formed, which is not affected by evaporating with concentrated hydrochloric acid. This compound is doubtless identical with the methylphenylurazole, melting at 183° to 185°, made by Busch and Heinrichs,[1] by the action of nitrous acid on 1-phenyl-2-methyl-3,5-oxy-4-aminourazole. These writers ascribed the isomeric urazine formula,

$$
\begin{array}{c}
\mathrm{C_6H_5N\!-\!\!-\!N} \\
\mathrm{OC\!\diagup \quad\quad \diagdown\!COCH_3,} \\
\mathrm{H\!-\!N\!-\!\!-\!N\!-\!H}
\end{array}
$$
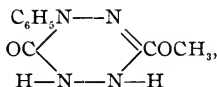
to this amino body, but this is clearly wrong, for two reasons. First, such a urazine should be soluble in alkalies, while their compound was insoluble ; this we should expect if it had the above urazole formula. Secondly, it could not be a methoxy derivative, for both their so-called '' urazine'' and the phenylmethylurazole made from it are very stable towards acids (hydrochloric acid).

The isomeric 1-phenyl-4-methylurazole was made by a method which could not give the 2-methyl compound. When phenylsemicarbazide is heated with methylacetylurea to 200° C. the reaction may be represented by the following :

$$
\begin{array}{c}
\mathrm{C_6H_5N\!-\!\!-\!\!-\!NH} \\
\mathrm{\overset{..}{H} \quad\quad |} \\
\mathrm{CH_3CONH\,CO \quad CO} \\
| \quad\quad | \\
\mathrm{CH_3N\,H\ NH_2}
\end{array}
$$
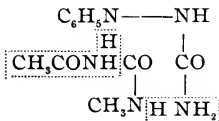
This compound melts at 225° and is stable toward concentrated hydrochloric acid at 100°. So phenylurazole, upon alkyla-

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[1] Busch and Heinrichs : Ber. d. chem. Ges., **33,** 455.

tion by means of potassium hydroxide and methyl iodide, gives 2-alkyl derivatives, and we shall use this method to prepare other homologues.

It might be thought surprising that in the alkylation of phenylurazole by potassium hydroxide and methyl iodide no methylation takes place at 4.

$$C_6H_5C \underset{OAg}{\overset{NH}{<}} + C_2H_5I = C_6H_5C \underset{O}{\overset{NHC_2H_5}{<}} + AgI.^2$$

Here we have alkylation on the nitrogen which is doubly linked to the $=COM$ group, and this reaction was formerly[3] thought to depend upon the addition of methyl iodide to the double bond and a subsequent loss of sodium iodide :

$$C_6H_5C \underset{ONa}{\overset{NH}{<}} + CH_3I = C_6H_5C{\overset{NHCH_3}{\underset{ONa}{-I}}} =$$

$$C_6H_5C \underset{O}{\overset{NHCH_3}{<}} + NaI.$$
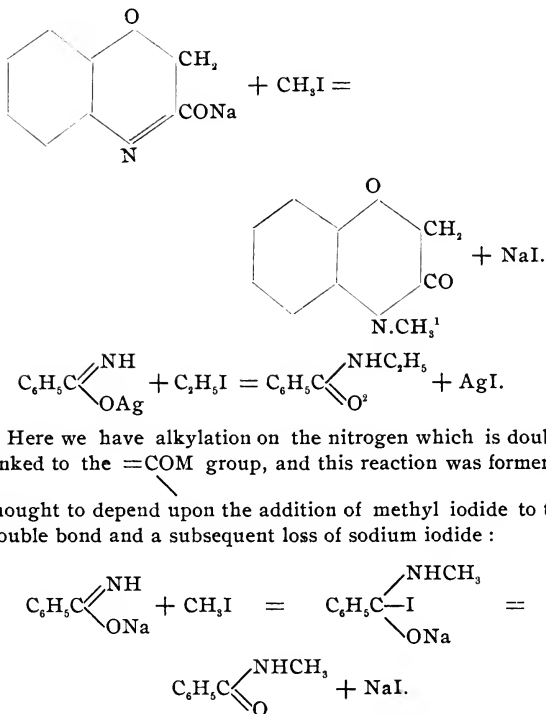
Nef[4] has recently shown that in all cases of methylation by

[1] Wheeler : This JOURNAL, **20**, 560.
[2] Wheeler : *Ibid.*, **21**, 185.
[3] Nef : Ann. Chem. (Liebig), **266**, 62 ; **280**, 287.
[4] Nef : *Ibid.*, **309**, 126.

means of methyl iodide there is first a dissociation into methylene, $CH_2=$, and hydriodic acid. The hydriodic acid may displace the metal and the methylene acts at the most favorable position, which, in the case of phenylurazole, happens to be at 2. Furthermore, if phenylurazole has the formula V., since there is no hydrogen at 4, we cannot have methylation at that place unless we assume the addition of water or hydriodic acid to the double bond between 3 and 4. Another similar case occurs in the methylation of 3-methyl-2,6-oxy-7-hydro-8-chlorpurine (3-methylchlorxanthine), which yields 8-chlortheobromine, and of 3-methyl-2,6-oxy-7-hydropurine (3-methylxanthine), which yields theobromine.[1]
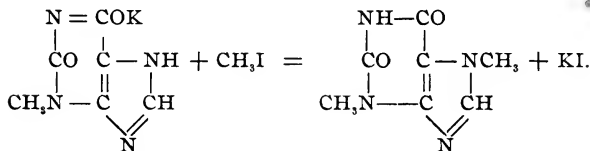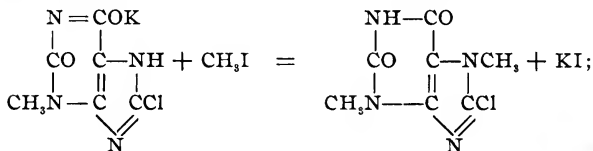
The methylation takes place at 7 and not at all at 1 ; hence the reaction cannot depend upon the addition of methyl iodide to the double bond between 1 and 6, and Nef's explanation seems to clear up the reaction.

If the above formula for phenylurazole be correct, we should expect two series of acyl derivatives—N- and O-acyl derivatives. The N-derivatives are acid amides and are comparatively stable. But the oxyacyl derivatives are really acid anhydrides, and we should expect them to be readily hydrolyzed by alcohol and water. This I have found to be the case. When the silver salt of phenylurazole is treated with acetyl chloride in benzene solution in the cold, a reaction slowly takes place and the odor of acetyl chloride disappears.

[1] E. Fischer and Ach : Ber. d. chem. Ges., **31**, 1980.

From the benzene solution there is obtained an oil having the constitution

$$C_6H_5N\text{——}NH$$
$$OC \quad COCOCH_3.$$
$$N$$
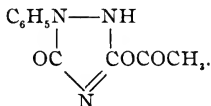
This, on boiling with alcohol a few minutes, or on standing in water solution, gives pure phenylurazole, melting at 264°. The isomeric 2-acetylphenylurazole is formed by the action of acetic anhydride on phenylurazole and is purified by crystallization from water and alcohol, and the neutral 2,3-diacetyl-1-phenylurazole is so sensitive to the action of water that it must be crystallized from some solvent like benzene. When crystallized from hot water it loses the O-acetyl group at 3 to give the acid 2-N-acetyl-1-phenylurazole.[1] This is a fine example, showing how much more stable the N-acyltriazoles, urazoles, etc., are than the O-derivatives. Bailey and Acree[2] showed that most of the 3-hydroxy-5-alkyltriazole-1-propionic acids have the enol structure. With diazomethane they give methoxytriazoles, which give methyl chloride when treated with concentrated hydrochloric acid. Hence we should expect their O-acetyl and benzoyl derivatives to be readily hydrolyzed by hot water, and this is indeed the case. When the 3-oxyacetyl-5-styryltriazole-1-propionic acid, melting at 168°, or ethyl 3-oxyacetyl-5-phenyltriazole-1-propionate, which melts at 80°, is boiled one hour with 75 per cent alcohol and the solution is cooled, there is obtained a precipitate of the pure 3-hydroxy-5-styryltriazole-1-propionic acid, which melts at 243°, or ethyl 3-hydroxy-5-phenyltriazole-1-propionate, which melts at 172°, respectively, showing that there is complete hydrolysis of these acyl derivatives.

Rupe and Labhardt[3] found that 1-phenyl-5-oxyacetyltriazole by evaporation with alcohol loses the acetyl group and gives the 1-phenyl-5-oxytriazole,

[1] Thiele and Schluessner : Ann. Chem. (Liebig), **295**, 171.
[2] Bailey and Acree : Ber. d, chem. Ges., **33**, 1520.
[3] Rupe and Labhardt : Ber. d. chem. Ges., **33**, 233.

$$C_6H_5N\text{---}N$$
$$HOC \quad CH$$
$$N$$
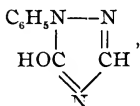
which melts at 178° to 181°; without doubt the acetyl was joined to the oxygen at 5.

Dains[1] attempted to prepare isoacylureas of the type

$$RNH$$
$$\qquad COCOR$$
$$RN$$
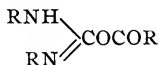
by the addition of acetic acid, etc., to *o*-carboditolylimide. Instead, the product of hydrolysis, *o*-carbtoluide,

$$(C_7H_7NH)_2CO,$$

was obtained, as the intermediate isoacylurea is too easily hydrolyzed. N-benzoyldiphenylurea,

$$C_6H_5CO$$
$$|$$
$$C_6H_5N\text{---}CONHC_6H_5,$$
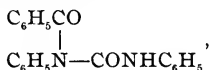
on the other hand, is very stable toward alcohol and water.

Dr. J. H. Ransom,[2] of Purdue University, writes me that when he boiled N-benzoylcarbonyl-*o*-aminophenol for one hour with water, the unchanged body, which melts at 174°, was recovered.

In acetylisatin,
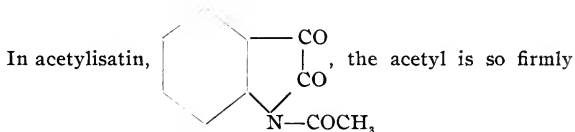
the acetyl is so firmly bound to the nitrogen that it gives acetylisatinic acid,[3]
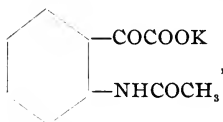
[1] Dains: J. Am. Chem. Soc., **21**, 136.
[2] Ransom: This JOURNAL, **23**, 20.
[3] Baeyer and Oekonomides: Ber. d. chem. Ges., **15**, 2100.

when treated with potassium hydroxide solution.   1-Benzoyl-
α-pyridone, when boiled with hydrochloric acid, gives

$$C_6H_5CONHCH = CH—CH=CHCOOH.$$
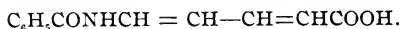
From these facts it is evident that the N-acyl derivatives of
urazoles, triazoles, etc., or any compounds with the group

$$—CO—NH— \quad \rightleftharpoons \quad —N=C(OH)—$$
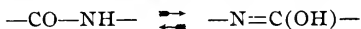
are much more stable than the O-acyl derivatives, the latter
being readily hydrolyzed [by alcohol or water, as most other
acid anhydrides are.

The phenylurazole used for this work was prepared by the
action of alkalies on the dicarbethoxyphenylsemicarbazide,
which substance was obtained directly in two modifications.
One modification has the melting-point 172°; the other, the
melting-point 154°.   When the product melting at 172° is re-
crystallized from water several times the melting-point is low-
ered to 154°, and this form, when cooled, melts again at 172°.
A sample of this product melting at 154° was mixed with a
sample of the product melting at 154° which was obtained di-
rectly, but there was no change in the melting-point.
Whether we have here the enol and keto tautomerism
described by Claisen,[1] Wislicenus,[2] Gutzeit,[3] Bailey and
Acree,[4] and others, must be decided by further work.

Work is now being carried forward on urazole- and thio-
urazole-1-propionic acids with Dr. J. R. Bailey, of Texas, and
on 1-phenyl-3,5-dithiourazoles and 1-phenyl-3(or 5)-thio-5
(or 3)-oxyurazoles in this laboratory.   We shall especially
investigate the molecular conductivities of these compounds
and their salts.   We ask that this work be left to us.

EXPERIMENTAL.

Phenylsemicarbazide.—This substance was prepared accord-
ing to Widman's[5] method.   To 20 grams phenylhydrazine
and 15 grams acetic acid in 250 cc. water kept at —5° was added

[1] Claisen : Ann. Chem. (Liebig), **277**, 188 ; **291**, 25.
[2] Wislicenus : *Ibid.*, **291**, 147.
[3] Gutzeit : Ber. d. chem. Ges., **26**, 2795 ; Ann. Chem. (Liebig), **285**, 35, 61, 108.
[4] Bailey and Acree : Ber. d. chem. Ges., **33**, 1520.
[5] Widman : *Ibid.*, **26**, 2613.

the theoretical amount of potassium cyanate in a small amount of cold water. The phenylsemicarbazide precipitates out immediately, and upon recrystallization from alcohol has the melting-point 172°. Yield, 23.5 grams.

Dicarbethoxyphenylsemicarbazide.—This substance was made by boiling 5 grams phenylsemicarbazide with 3.5 grams chlorcarbonic ether in 50 cc. acetic ether for four hours, with a return condenser. Upon cooling, the substance precipitates out as a white solid, melting undecomposed, at 172°. When mixed with a sample of phenylsemicarbazide, melting at 172°, the melting-point was lowered to 140°–150°. When recrystalized from water several times it had the melting-point 154°, and when solidified it melted again at 172°. One sample of this dicarbethoxy compound, made as above, failed to precipitate from the acetic ether till this was evaporated. The compound then had the melting-point 154°, and when mixed with the product melting at 154° obtained by recrystallization from water, the melting-point was not changed. Whether we are dealing here with tautomeric enol and keto forms or with physical modifications of the same substance, as in the case of benzophenone,[1] must be decided by further work.

Analysis :

I. 0.2780 gram substance (m. p. 172°), gave 0.5370 gram CO_2 and 0.1490 gram H_2O.

II. 0.2395 gram substance (m. p. 154°), gave 0.4608 gram CO_2 and 0.01274 gram H_2O.

	Calculated for $C_{13}H_{17}N_3O_5$.	I.	II.
		Found.	
C	52.83	52.37	52.37
H	5.82	5.95	5.87

Phenylurazole. — When this dicarbethoxy compound is heated with alkalies it gives phenylurazole. Eight grams of the ester heated four hours at 100° with an excess of caustic soda, when cooled and acidified, gave 4.5 grams phenylurazole, melting with decomposition at 264°. If the ester is treated only a short time in the cold with caustic soda and then acidified, no precipitate is formed. The phenylurazole

---

[1] Zincke : Ann. Chem. (Liebig), **159**, 377; R. Meyer : Ber. d. chem. Ges., **22**, 550.

is difficultly soluble in cold water and ether, but readily soluble in hot alcohol. With an alcoholic solution of ferric chloride it gives a dirty violet color, which proves the presence of an enol group. It is a strong monobasic acid, giving a sharp reaction with one molecule of caustic potash, using phenolphthaleïn and forming mono-silver and barium salts.

0.2316 gram phenylurazole required 9.08 cc N/7 caustic soda instead of the calculated 9.15 cc.

Silver Salt.—This is made by adding the calculated amount of silver nitrate to the neutral sodium salt and boiling the solution. The precipitate is then easily filtered. It is very stable toward light, is easily soluble in ammonium hydrate, but insoluble in dilute nitric acid. It melts at 252° with decomposition, giving off fumes having a strong isocyanate odor.

0.2143 gram silver salt gave 0.0816 gram silver.

	Calculated for $C_8H_6N_3O_2Ag$.	Found.
Ag	37.90	38.08

Barium Salt.—By titrating 0.5 gram phenylurazole with 29.5 cc. N/10 barium hydroxide, using phenolphthaleïn as indicator, and evaporating nearly to dryness and cooling, the barium salt crystallized out in plates, which were washed with alcohol and dried in the air. It decomposes at 280° to 300° without charring. There are 2 molecules of water of crystallization.

0.1970 gram substance heated five hours at 120° lost 0.0136 gram.

0.2065 gram salt required 7.82 cc. N/10 potassium sulphate and N/10 potassium bichromate to precipitate the barium and give a yellow solution.

	Calculated for $(C_8H_6N_3O_2)_2Ba + 2H_2O$.	Found.
H_2O	6.86	6.90
Ba	26.16	26.01

1-Phenyl-2-methyl-3-hydroxyurazole,

$$\begin{array}{cc} C_6H_5N{-}{-}NCH_3 \\ | \quad\quad | \\ OC \quad COH \\ \diagdown\,\diagup \\ N \end{array}$$.—This
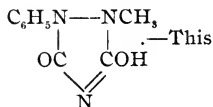
substance was first made by Busch and Heinrichs[1] by the action of nitrous acid on 1-phenyl-2-methyl-4-aminourazole,

$$
\begin{array}{c}
\mathrm{C_6H_5N\!\!-\!\!-\!\!-NCH_3} \\
\mid \qquad\quad \mid \\
\mathrm{OC} \quad\; \mathrm{CO} \\
\diagdown\diagup \\
\mathrm{N\!-\!NH_2}
\end{array}
$$
,
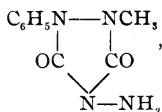
(see theoretical part). By heating phenylurazole in alcoholic potash with one molecule of methyl iodide three hours, with a return condenser, evaporating off the alcohol and acidifying, a precipitate of fine needles, which melt at 183°, is obtained. The substance is readily soluble in alkalies, ether and alcohol, and is somewhat soluble in cold water. By evaporating to dryness twice with concentrated hydrochloric acid, the body which melts at 183° is recovered unchanged, showing that the methyl group is attached to nitrogen and does not form the methoxy group, as Busch and Heinrichs supposed. This same methyl derivative, mixed with phenylurazole, is obtained by boiling the silver salt of phenylurazole with an alcoholic solution of methyl iodide with a return condenser for five hours. The substance is a monobasic acid giving a sharp reaction with 1 molecule of sodium hydroxide (phenolphthaleïn), and forming a mono-silver salt.

0.1382 gram substance required 7.26 cc. N/10 sodium hydroxide instead of 7.23 cc., calculated.

Analysis :

0.1096 gram substance gave 22.35 cc. nitrogen at 24° and 736 mm.

	Calculated for $C_9H_9N_3O_2$.	Found.
N	22.03	22.12

Silver Salt.—This is made by adding silver nitrate to the solution of the sodium salt and boiling. The precipitate is then readily filtered, and when dry melts at 250°, giving off strong fumes of an isocyanate. The salt is very soluble in ammonium hydrate, but insoluble in dilute nitric acid. When heated fifteen minutes with hydrochloric acid, filtered from

[1] Busch and Heinrichs : Ber. d. chem. Ges., **33**, 455.

the silver chloride, and evaporated, crystals of the 1-phenyl-2-methylurazole, which melts at 183°, are obtained.

Analysis :

0.1566 gram silver salt gave 0.0570 gram silver.

	Calculated for $C_9H_8N_3O_2Ag$.	Found.
Ag	36.20	36.40

1-*Phenyl-4-methylurazole*,

$$
\begin{array}{c}
C_6H_5N{-}{-}N \\
\quad | \qquad || \\
OC \quad COH \\
\diagdown \diagup \\
NCH_3
\end{array}
$$

.—This was made

by a method which could not give the 1-phenyl-2-methylura-zole. When molecular proportions of phenylsemicarbazide and methylacetylurea are melted together and heated two hours to 200°, ammonia and acetic acid are evolved and the mass becomes pasty. By dissolving in warm, dilute alcohol, cooling and filtering, 20 per cent of 1-phenyl-4-methylurazole is obtained. Its melting-point is 225°. The compound gives a violet color with alcoholic ferric chloride and gives mono-sodium and silver salts. By repeated evaporation with concentrated hydrochloric acid the melting-point is not changed. As the methyl group in this compound can only be at 4, it is evident that the methylation of phenylurazole by means of methyl iodide and alkalies takes place at 2, the hydrogen at this place seeming to be replaced more readily by methyl, acetyl, etc.

Analysis :

I. 0.1029 gram substance gave 21.5 cc. nitrogen at 28° C. and 730 mm.

II. 0.0420 gram substance gave 8.5 cc. nitrogen at 27° C. and 732 mm.

	Calculated for $C_9H_9N_3O_2$.	I.	II.
		Found.	
N	22.02	22.00	21.50

Silver Salt.—This was made by adding the requisite amount of silver nitrate to a solution of the neutral sodium salt, and boiling. Upon filtering and drying, there is obtained a stable silver salt, which melts at 225°, with decomposition, giving an isocyanate odor.

Analysis :

I. 0.1067 gram silver salt gave 0.0393 gram silver.

II. 0.0516 gram silver salt gave 0.0191 gram silver.

	Calculated for $C_9H_8N_3O_2Ag$.	Found.	
		I.	II.
Ag	36.24	36.83	37.01

$$\begin{array}{c} C_6H_5N\!\!-\!\!-NH \\ | \qquad | \\ OC \qquad COC_2H_5 \\ \diagdown\!\!\diagup \\ N \end{array}$$

1-Phenyl-2-hydro-3-ethoxyurazole, .—When the silver salt of phenylurazole, suspended in benzene, is treated with ethyl iodide in the cold for ten days, the reaction is complete. Upon filtering and evaporating off the benzene there is obtained an oil that gradually solidifies. Its melting point is about 141°. It is easily soluble in ether, benzene, alcohol, and slightly soluble in ligroin, but is insoluble in water and alkalies. Even boiling with concentrated caustic potash fails to effect solution. On the other hand, by evaporation with alcoholic hydrochloric acid, the ethoxy group is saponified and pure phenylurazole, melting at 264°, is obtained. Boiling this ethoxy compound with alcoholic potash and methyl iodide, with a return condenser, fails to methylate at the position 2. Upon evaporation, the oily ethoxy compound is recovered, which yields, when treated with hydrochloric acid, the phenylurazole that melts at 263°. An attempt was made to prepare this ethoxy compound by letting phenylurazole stand for one month in absolute ethyl alcohol containing 3 per cent of gaseous hydrochloric acid, but only unchanged phenylurazole was obtained. The question of the constitution of phenylurazole depends upon whether this ethoxy derivative is soluble in alkalies or not. A substance with the above formula cannot be soluble in alkalies, whereas the isomeric 1-phenyl-3-ethoxy-4-hydrourazole[1] is readily soluble in alkalies forming salts :

$$\begin{array}{c} C_6H_5N\!\!-\!\!-N \\ | \qquad \| \\ MOC \qquad COC_2H_5 \\ \diagdown\!\!\diagup \\ N \end{array}$$

, and is reprecipitated by acids.

[1] Wheeler : J. Am. Chem. Soc., **22**, 377 (1900).

Analysis:

0.3616 gram substance gave 19.3 cc. nitrogen at 29° C. and 732 mm.

	Calculated for $C_{10}H_{11}N_3O_2$.	Found.
N	20.59	20.10

1-Phenyl-2-hydro-3-oxyacetylurazole,

$$\begin{array}{c} C_6H_5N\text{——}N \\ | \qquad | \\ OC \qquad COCOCH_3 \\ \diagdown\diagup \\ N \end{array}$$

This compound was made by allowing acetyl chloride to act upon the silver salt of phenylurazole in benzene solution in the cold. By filtering off the silver chloride, and evaporating off the benzene and acetyl chloride, an oil was obtained that would not solidify.

Analysis:

0.1301 gram substance gave 23.36 cc. nitrogen at 22° C. and 724 mm.

	Calculated for $C_{10}H_9N_3O_3$.	Found.
N	19.21	19.35

When it was dissolved in boiling dilute alcohol and heated for a few minutes, or if the water solution was allowed to evaporate in a desiccator, only the phenylurazole melting at 263° was obtained. Hot acids and alkalies saponify the body almost instantly. By its method of formation this compound must be the 1-phenyl-2-hydro-3-oxyacetylurazole, and the iso-meric N-derivative,[1] which melts at 175°, must be the 1-phenyl-2-acetyl-3-hydroxyurazole, while the diacetylphenyl-urazole, melting at 164°, must be the 1-phenyl-2-acetyl-3-oxy-acetylurazole. By boiling with water it loses, as we should expect, the O-acetyl at 3, giving the 2-N-acetylphenylurazole melting at 175°.

When 3-oxyacetyl-5-styryltriazol-1-propionic acid, which melts at 168°[2] is boiled two hours with a return condenser with 50 per cent alcohol, 3-hydroxy-5-styryltriazole-1-pro-pionic acid, which melts at 243°, precipitates out on cooling.

[1] Thiele and Schleussner : Ann. Chem. (Liebig), **295**, *171* ; Cuneo : Centrbl., 1898. I., 38.

[2] Bailey and Acree : Ber. d. chem. Ges., **33**, 1520.

When the ethyl 3-oxyacetyl-5-phenyltriazole-1-propionate, which melts at 80°, is treated in the same way, there is obtained the ethyl 3-hydroxy-5-phenyltriazole-1-propionate, which melts at 168°. Since these acetyl derivatives have been proved to be oxy compounds, this easy hydrolysis is to be expected.

The comparison of the relative amount of hydrolysis of the isomeric N- and O-acyl derivatives of isatine, phenylurazole, phenyl mono- and dithiourazoles, and of urazole fatty acids will be taken up and studied quantitatively, and we wish to have this work left to us.

Diphenylurazine.—Work was started to determine the constitution of diphenylurazine. This compound was first made by Pinner[1] by heating phenylsemicarbazide, and then by Heller[2] by heating phenylcarbazinic ester. Pinner ascribed to this compound the symmetrical constitution :

$$C_6H_5N—NH—CO$$
$$OC—NH—N—C_6H_5$$
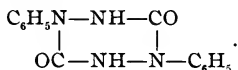
Such a compound should be a dibasic acid and give a disilver salt. But diphenylurazine is a monobasic acid, giving a violet color with alcoholic ferric chloride, combining with 1 molecule of caustic soda, and forming a monosilver salt, although giving a diacetyl derivative. Hence we seem to have a compound with an unsymmetrical constitution and it can be only

I.
$$C_6H_5—N—N—H$$
$$OC \qquad C.OH$$
$$C_6H_5—N—N$$

or II.
$$C_6H_5—N—N$$
$$\qquad\qquad C.OH$$
$$OC—N—NH.C_6H_5$$
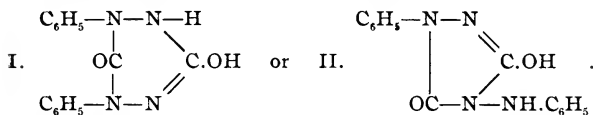
Recent work by Rupe and Gebhardt[3] seems to confirm formula I, and we will not continue this work.

Pinner states that diphenylurazine, which melts at 264°, is changed by boiling alkalies into an isomeric form, which melts at 231°. This is a mistake. When boiled with an ex-

[1] Pinner : Ber. d. chem. Ges., **21,** 1225.
[2] Heller : Ann. Chem. (Liebig), **263,** 382.
[3] Rupe and Gebhardt : Ber. d. chem. Ges., **32,** 10.

cess of caustic potash for one hour and acidified, only pure diphenylurazine, melting at 264°, was obtained.

Diphenylurazine does not titrate sharply against one molecule of sodium hydroxide (phenolphthaleïn).

0.3055 gram substance required 7.46 cc. N/7 caustic potash, instead of 7.97 cc., calculated.

0.1568 gram substance required 3.91 cc. N/7 caustic potash, instead of 4.09 cc., calculated.

Silver Salt.—When silver nitrate is added to a solution of the sodium salt of diphenylurazine and boiled, an amorphous precipitate of the monosilver salt is obtained.   This is fairly stable toward light, and when heated darkens at 188° and decomposes at 204°, giving off isocyanate fumes.

Analysis :

0.2264 gram substance gave 0.0648 gram silver.

	Calculated for $C_{14}H_{11}N_4O_2Ag$.	Found.
Ag	28.77	28.62

UNIVERSITY OF UTAH,
    December 1, 1901.

THE CONVERSION OF ORTHOPERIODIC ACID INTO NORMAL PERIODIC ACID.

BY ARTHUR B. LAMB.

While perchloric acid, its anhydride, monohydrate, and dihydrate are known, only the dihydrate of periodic acid has as yet been described.   Bengiesser,[1] to be sure, states that the crystalline acid, H_5IO_6, loses its water of crystallization at 160° and does not decompose into oxygen and iodic anhydride until a temperature af 190° is reached.   In other words, he states that periodic anhydride is formed at 160° and remains undecomposed at a temperature as high as 190°. Langlois[2] found that only at 200° is all the water eliminated, iodic anhydride and oxygen being formed at the same time.

Rammelsberg,[3] however, studied the effect of heat on the acid most carefully and arrived at quite different results.   He

[1] Ann. Chem. Pharm., **17**, 254.
[2] J. prakt Chem., **56**, 36.
[3] *Ibid.*, **103**, 281.

found that between 130°, the melting-point of the acid, and 136°, slow decomposition takes place, iodic anhydride, oxygen, and water being formed. From this he concludes that the preparation of periodic anhydride in this way is impossible.

It seemed probable, however, that if the acid were heated in a vacuum it might be possible to separate the point of dehydration from that of decomposition.

In the vacuum drying apparatus used, a constant temperature was maintained by the vapor of a boiling liquid. This temperature was, of course, variable at will by a change of liquids. The air entering the apparatus was dried by passing through tubes containing, first, calcium chloride and soda lime, then sulphuric acid, and finally, phosphoric anhydride.

The dihydrated acid, H_5IO_6, was prepared as follows: Chlorine was passed into a concentrated solution of sodium iodate and hydrate. Trihydrogen sodium periodate,

$$Na_2H_3IO_6,$$
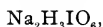
was thereby precipitated (Magnus and Ammermüller).[1]

Silver nitrate converted an acid solution of this salt into the silver salt, from which the free acid was secured by treatment with bromine (Kämmerer).[2] The resulting aqueous solution of the acid, after having been evaporated as completely as possible on the water-bath, was dried to constant weight by standing several days over strong sulphuric acid and phosphoric anhydride. To establish the purity of this acid it was analyzed. The original distillation method of Bunsen[3] was used, not, however, until fruitless attempts had been made to secure concordant results by the method of analysis used by Kimmins.[4]

 I. 0.0464 gram liberated 0.15888 gram iodine.

 II. 0.0493 gram liberated 0.16350 gram iodine.

	Calculated for H_5IO_6.	Found. I.	II.
I	55.60	55.32	55.29

[1] Pogg. Anu., **28**, 514.
[2] J. prakt. Chem., **79**, 94.
[3] Ann. Chem. (Liebig), **86**, 265.
[4] J. Chem. Soc. (London), **51**, 361; **55**, 154.

A portion of the acid had been tested with silver nitrate and nitric acid, but only a trace of iodic iodine had been found.

Taking samples of this acid, using water in the vapor jacket of the drying apparatus, and a pressure of 12 mm., a constant weight was in general secured after heating from twenty to twenty-five hours. The drying process was interrupted when the loss, after several hours, amounted to but a fraction of a milligram. This was necessary since sublimation became apparent upon the walls of the drying chamber after ten or twelve hours of heating, and experiment showed that such slight losses would continue indefinitely.

No.	Substance heated. Gram.	Loss in weight. Gram.	Loss in weight. Per cent.
I.	0.4055	0.0642	15.83
II.	0.4842	0.0747	15.43
III.	0.8673	0.1357	15.59

Mean, 15.62

	Per cent.
Calculated loss for H_3IO_5	7.91
" " " HIO_4	15.74
" " " I_2O_7	19.79

These numbers point with certainty to the composition HIO_4.

Qualitative tests of this dehydrated acid showed the presence of slightly more iodic iodine than was present in the original acid. To confirm the above conclusions, based on the loss of weight, analyses from samples of the above dehydration, experiment III., were made :

No.	Acid. Gram.	Iodine liberated. Gram.	Iodine liberated. Per cent.
I.	0.0966	0.37761	65.16
II.	0.0500	0.19651	65.50
III.	0.0677	0.26407	65.22

Mean, 65.29

	Per cent.
Calculated per cent of iodine in H_3IO_5	60.45
" " " " " HIO_4	66.12
" " " " " I_2O_7	69.37

Analysis therefore confirms the conclusion that the acid formed by the dehydration method under the above conditions was the compound represented by HIO_4.

This normal periodic acid was white or slightly yellowish in color. When dropped into water, sufficient heat was generated to occasion audible hissing.

Higher temperatures were now tried, in the hope of securing periodic anhydride. Toluene, boiling at $110°$, was substituted for water in the drying apparatus. Sublimation became more apparent on the walls of the drying chamber, but no loss in weight occurred beyond that evidently due to this cause. Tests indicated the presence of somewhat more iodic iodine than was present in the acid dried at $100°$.

Substituting xylene, boiling at $138°$, marked sublimation occurred, accompanied by a rapid loss in weight. Large amounts of iodic anhydride were now found to be present. This agrees with the statement of Rammelsberg quoted above.

To determine whether a vacuum had any detrimental effect at these high temperatures, a sample of the normal acid was treated at atmospheric pressure in the drying apparatus, using toluene in the vapor jacket. The acid lost rapidly in weight, and much iodic anhydride was formed. After thirty hours' heating the loss in weight indicated that if partial decomposition had taken place into iodic anhydride, oxygen, and water, approximately 40 per cent of the resultant mixture should be iodic anhydride. Analyses were made by Bunsen's method, and the relative amounts of iodic anhydride and normal periodic acid were calculated on the assumption that nothing else was present.

I. 0.1332 gram liberated 0.48918 gram iodine = 31.1 per cent of I_2O_5.

II. 0.1094 gram liberated 0.40033 gram iodine = 33.3 per cent of I_2O_5.

The percentage amounts of iodine in iodic anhydride and in normal periodic acid are so nearly the same (76.1 per cent and 66.1 per cent, respectively) that the slightest difference in the amount of iodine liberated was magnified many times in the calculation.

In addition to heat, several other means were employed to dehydrate normal periodic acid, but without success. Acetyl chloride added to the acid reacted violently even at —20° ; if the acid was added to the chloride the reaction was less energetic. A clear, cherry-red solution was obtained in either case, which, added to water, showed complete reduction to the iodic condition. If acetyl chloride were added to a solution of the normal acid in glacial acetic acid, a white flocculent precipitate appeared. This also, when filtered off and washed, showed complete reduction to the iodic condition. When dried in a vacuum at 100° and analyzed, the following numbers were obtained.

0.0844 gram liberated 0.25191 gram iodine.

	Calculated for I_2O_5.	Found.
I	76.1	74.6

Acetic anhydride also reacts with the acid vigorously at ordinary temperatures, but slowly in the cold. Evolution of a gas takes place and the reaction-product showed, on the addition of water, complete reduction to the iodic condition.

Anhydrous perchloric acid also decomposed the acid, even at low temperatures.

Repeated attempts were also made to secure the intermediate hydrate, H_3IO_5, by drying.

1. At a temperature of 67° and a pressure of 17 to 18 mm.
2. At a temperature of 55° to 64° and a pressure of 27 mm.[1]
3. At a temperature of 44° to 49° and a pressure of 24 mm.

In all three experiments the point corresponding to the hydrate, H_3IO_5, was passed without the least indication of the formation of a definite compound, though in the two latter experiments the rate of dehydration was exceedingly gradual ; in the second, fifty hours, in the third, one hundred hours being required to pass the point in question. It appears impossible to secure this intermediate hydrate by simple drying.

The author wishes to thank Prof. A. Michael for his suggestion of the research and valuable assistance in its execution.

TUFTS COLLEGE, MASS.

[1] In the second and third experiments a water-bath was used as jacket for the dehydration vessel, which latter contained, besides the substance, a thermometer and a manometer.

A SIMPLE APPARATUS FOR DEMONSTRATING THE MANUFACTURE OF WATER-GAS.

BY C. E. WATERS.

The great advantage of being able to demonstrate the manufacture of water-gas as a lecture experiment is so obvious that a form of apparatus was devised which works very successfully. A piece of heavy, two-inch iron pipe is provided with caps, screwed on the ends. Into the lower one is screwed a piece of pipe, of one-fourth inch bore, bent at a right angle, and connected by a rubber tube with an oxygen-cylinder. About 3 inches above the base, is screwed in a quarter-inch pipe about 2 feet 6 inches or three feet long. To this is attached an Erlenmeyer flask, which serves as the steam generator. By a simple arrangement of spring pinch-cocks the steam can be passed through the pipe or allowed to escape into the air. Into the upper cap is screwed a short piece of half-inch pipe, which has a quarter-inch hole bored through close to the upper end. This hole may be closed by screwing down a cap which is provided with a suitable handle. A large pair of gas-pliers could be used instead of the handle. Into a second hole in the upper cap is screwed the delivery tube of quarter-inch pipe, which carries the gas into a pneumatic trough, where it may be collected in cylinders. It is advisable to use a glass tube at the outer end of the delivery tube, and to avoid burning the rubber connection it is well to have the pipe bent into a ⋃, which dips under cold water contained in a crystallizing-dish.

The large pipe is sheathed inside and out with several layers of asbestos paper, and the caps are provided inside with perforated disks of asbestos board to protect the iron as much as possible. The bottom of the pipe is also filled with fragments of tile to a depth of 2 inches.

The experiment is carried out in the following manner: A fuse made of loosely-twisted cotton string is pushed in through the side opening. Then small fragments of charcoal, fine
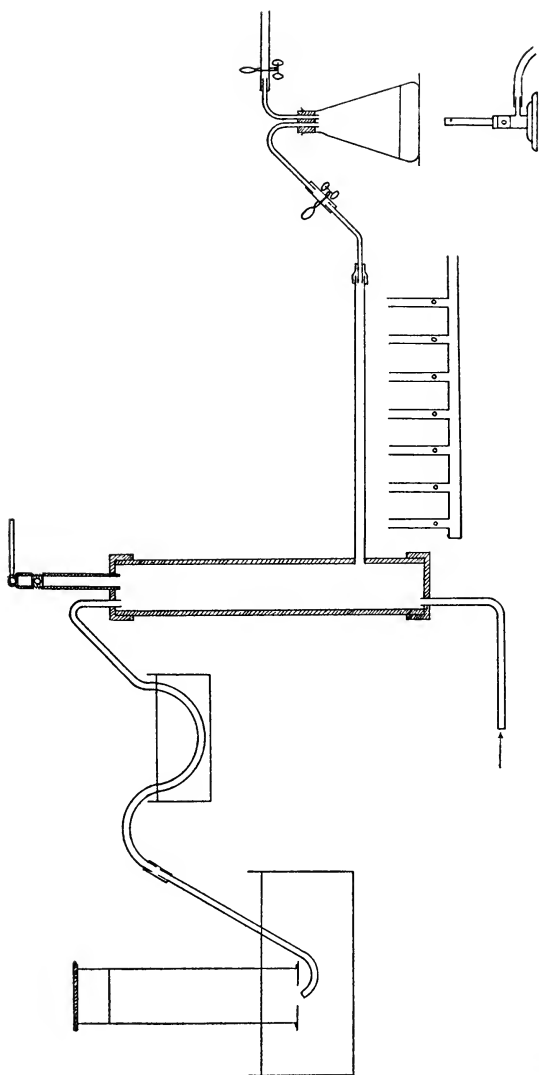
coke, and finally $\frac{1}{2}$ to $\frac{3}{4}$-inch pieces of coke are poured in at the top until the large pipe is nearly filled. The upper cap is re-placed and the whole is then supported on a stand, using one small ring at the bottom and a larger one at the middle. It is well to use a clamp at one of the upper pipes also. It is placed close to the end of a combustion furnace, and at such a height that the horizontal tube will lie in the trough when screwed into place. The Erlenmeyer flask is placed in position and the water heated to boiling by a small flame. The furnace should also be lighted. When all is ready the fuse is lighted, a slow current of oxygen is passed in through the tube at the bot-tom, the lateral tube is screwed in place, and all connections are made. For the "hot blast" the hole in the side of the upper tube should be open. An increased current of oxygen is passed in until the outer layer of asbestos becomes very hot. Then the oxygen is shut off, the upper opening closed, and by adjusting the pinch-cocks steam is passed through the horizontal pipe, which should be heated nearly to redness. As soon as this superheated steam reaches the hot coke there is quite a rapid evolution of gas, which is collected in cylin-ders. In a few moments no more comes over, and the steam is to be shut off from the furnace and the outer pinch-cock is opened ; the upper outlet is reopened, and oxygen is run in as before. The operation can, of course, be repeated until the coke is consumed.

The gas is at first clouded, but soon becomes clear. It burns with a pale-blue flame. It is a simple matter to enrich it by causing it to bubble through benzene, or some similar hydrocarbon, contained in a wash-bottle. Working on such a small scale, it is not to be expected that the gas would have the same composition as that made commercially. Analysis showed that it is true water-gas, and not simply carbon mon-oxide forced over by the entering steam. To make sure that the hydrogen was not formed in the superheating tube, we raised the temperature of this tube still further and passed the steam into water. The gas which was collected gave no evidence of containing hydrogen.

Analysis of Water-Gas.

	I.	II.	III.	IV.
CO_2	19.2	40.3	31.7	33.8
O_2	0.8	0.2	1.5	0.0
CO	43.8	19.0	27.4	31.1
H_2	27.1	29.1	31.3	29.1
N_2	9.1	11.4	8.1	6.0

These figures become more nearly comparable when recalculated on the basis of a mixture from which the carbon dioxide has been removed.

	I.	II.	III.	IV.
O_2	0.9	0.3	2.3	0.0
CO	52.6	32.3	41.1	46.7
H_2	32.5	49.5	47.0	43.7
N_2	10.9	19.4	12.2	9.0

The oxygen which was used was found to contain about 8 per cent of nitrogen. The varying proportions of carbon monoxide and hydrogen may be due to the considerably greater solubility of the former in water, which would make quite a difference when only small quantities of the water-gas are made.

JOHNS HOPKINS UNIVERSITY,
    December, 1901.

DICHLORACETYL PHOSPHIDE.

BY P. N. EVANS AND C. E. VANDERKLEED.

In a general survey of the classes of organic compounds one is struck by the fact that in spite of the recognized analogy in properties between the amines and phosphines, reference to the phosphorus derivatives corresponding to the acid amides is entirely lacking in most text-books, presumably on account of the very small number of representatives of this class known. Apparently only two of these bodies, which may appropriately be called *phosphides*, have been prepared and examined, namely, monochloracetyl phosphide[1] and trichloracetyl phosphide.[2]

The purpose of the work here presented was to add to our knowledge of this class of compounds.

[1] Steiner : Ber. d. chem. Ges., 8, 1178 (1875).
[2] Cloëz : Ann. chim. phys., [3], 17, 309.

Since the readiness of formation and the stability of these substances depend on the acid character of the organic radical and the basic properties of the PH_2 group, it can be foreseen that the phosphides will be less readily prepared and less stable than the corresponding amides, on account of the more weakly basic character of phosphorus than of nitrogen in the hydrogen compounds, and those phosphides will be most easily made whose organic radicals are most strongly acid.

Of the many methods used to prepare amides, the reaction involving the treatment of an acid chloride with ammonia takes place most vigorously and generally, and therefore the analogous method seemed most promising for the preparation of the phosphides ; and this was the reaction employed in the cases already successfully investigated, previously mentioned. Some preliminary experiments with phosphine (PH_3) and chlorides of some of the commoner acids by one of the authors have given unpromising results, solid phosphorus hydride being produced, but it is hoped to further examine these cases soon. It seemed desirable, therefore, for the sake of experience, to select an acid that might reasonably be expected to give positive results, and since mono- and trichloracetic acids had already given the desired products in other hands, the intermediate dichloracetic acid was selected. Acetic acid itself had presented difficulties under experiment, but the greatly increased acid character due to chlorination gave hope of better results with the chloracetic acids.

Preparation of Materials.

The materials required were dichloracetyl chloride, $CHCl_2COCl$, and gaseous hydrogen phosphide, PH_3.

Dichloracetyl Chloride.—This involved the preparation of potassium dichloracetate from potassium ferrocyanide and chloral hydrate by heating in water,[1] the liberation of dichloracetic acid from the potassium salt by means of hydrochloric acid gas,[2] and the conversion of the acid into the acid chloride by treatment with phosphorus trichloride.[3]

The details of the preparation were as follows :

[1] O. Wallach : Ber. d. chem. Ges., **10**, 1526 (1877).

[2] O. Wallach : *Ibid.*, **9**, 1213 (1876).

[3] R. Otto and H. Beckurts : *Ibid.*, **14**, 1618 (1881).

Potassium Dichloracetate.—One hundred and seventy grams potassium ferrocyanide and 115 grams chloral hydrate were dissolved in 500 cc. water in a flask with reflux condenser, and heated until the color of the ferrocyanide disappeared (about two hours), a green precipitate of a double cyanide of iron and potassium, $KFe(CN)_3$, separating and being filtered off from time to time to prevent bumping. When the reaction was complete the mixture was cooled and filtered, and then heated to prove that no further precipitation occurred. The filtrate was then evaporated to dryness on the water-bath and the potassium dichloracetate extracted from the potassium chloride with about 450 cc. strong alcohol in several portions ; the alcoholic extract was evaporated to dryness on the water-bath and the residue dried at 105°. The reaction is represented by the equation

$$2K_4Fe(CN)_6 + 3CCl_3CHO.H_2O =$$
$$3CHCl_2COOK + 3KCl + 2KFe(CN)_3 + 6HCN,$$
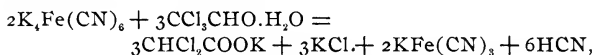
and the yield was about 70 per cent of the theoretical.

Dichloracetic Acid.—The dried potassium dichloracetate was placed in a piece of ordinary combustion tubing held nearly horizontal and connected by a long adapter at its lower end with a dry flask ; a current of dry hydrochloric acid gas was passed through from the upper end and the tube gently heated till the gas escaped from the flask ; then the temperature was raised till all the dichloracetic acid, boiling at 190°, had distilled into the flask. The yield was about 70 per cent of the theoretical.

Dichloracetyl Chloride.—Fifty grams of dichloracetic acid and 30 cc. phosphorus trichloride were warmed together with reflux condenser as long as hydrochloric acid was evolved, and then the dichloracetyl chloride, boiling at 107°, distilled off. The yield was about 60 per cent of the theoretical.

Gaseous Hydrogen Phosphide.—Two hundred and fifty grams potassium hydroxide were dissolved in 500 cc. strong alcohol and placed in a liter flask, and 50 grams yellow phosphorus added ; after displacing the air in the flask with illuminating gas, a gentle heat was applied and the gas, about 20 liters, conducted into a gas-holder for use. Prepared in this way it

is not spontaneously inflammable and contains about equal volumes of the phosphide and hydrogen.

Preparation of Dichloracetyl Phosphide.

The hydrogen phosphide, after being dried by passing through a tube about a meter long filled with soda-lime, was passed slowly through the dichloracetyl chloride contained in a small flask for several hours, the liquid becoming somewhat yellow and more and more viscous until the gas no longer passed through in bubbles but formed a channel. When this condition was reached, several times the volume of anhydrous ether, free from alcohol, was added. On standing some hours, with occasional shaking, the gummy mass was changed to a yellowish-white powder, which was filtered off, washed with ether, dissolved in a very small quantity of alcohol, again filtered and reprecipitated with ten or more volumes of ether, being allowed to stand several hours. The faintly yellow powder was filtered off, washed with ether, dried in a vacuum desiccator, and finally at 100°.

Attempts to prepare the phosphide by passing the gas into a solution of the acid chloride in ether and in benzene gave the product as a suspended powder, but the yield was poorer than when the solvents were not employed.

Analysis of the Product.

A qualitative examination showed charring on heating, with evolution of a substance with a phosphorus-like odor, and on ignition with copper oxide a bluish-green flame coloration, indicating the presence of carbon, phosphorus, and chlorine.

Quantitative estimations of phosphorus and chlorine were made to confirm the supposed formula, $CHCl_2COPH_2$, which corresponds to phosphorus 21.37 and chlorine 48.96 per cent.

Phosphorus was estimated by the Carius method and satisfactory figures obtained ; but the same method for the simultaneous estimation of chlorine gave variable results, in all cases lower than the proportion required by the formula, so the method of igniting in an open tube with lime was employed, with satisfactory results.

In the phosphorus estimation, the material (about 0.2 gram)

10–27

was heated in a sealed tube with fuming nitric acid and silver nitrate (for the chlorine) to 200° for eight hours, the silver chloride filtered out, the remaining silver precipitated with hydrochloric acid and removed, then the phosphoric acid precipitated with ammonium molybdate, and finally with magnesia mixture and weighed as pyrophosphate.

0.1530 gram substance gave 0.1218 gram $Mg_2P_2O_7$, corresponding to 22.2 per cent phosphorus. A second analysis gave practically the same result.

In the chlorine estimation the substance (about 0.05 gram) was mixed with lime and heated in a combustion tube for an hour or more, then the mixture dissolved in dilute nitric acid, filtered, and the chlorine precipitated as silver chloride with silver nitrate.

0.0493 gram substance gave 0.0932 gram AgCl, corresponding to 46.55 per cent chlorine; and 0.0479 gram substance gave 0.0930 gram AgCl, corresponding to 48.01 per cent chlorine.

These figures, while not as exact as desired, leave hardly a doubt as to the identity of the product examined.

Properties of the Phosphide.

Dichloracetyl phosphide is a faintly yellowish-white crystalline powder with a slight odor resembling the free acid and hydrogen phosphide, apparently due to slow decomposition due to moisture. Heated to 200° C., it chars without melting. It is nearly or quite insoluble in ether, benzene, chloroform, and petroleum ether; insoluble in cold water, but soon decomposed by it with evolution of hydrogen phosphide; very soluble in strong alcohol, the solution acquiring, after a time, a fruit-like odor, probably due to a decomposition resulting in the formation of the ethyl ester of the acid; in absolute alcohol it is very soluble without apparent decomposition.

The preparation of other acid phosphides by similar reactions is being carried out successfully and will be reported in a later paper.

LAFAYETTE, INDIANA,
  December, 1901.

On the Present State of the Chemistry of Albumin.[1]

The chemical investigation of the vegetable and animal organs has shown that certain elements and atomic groups are present in all living parts. We must assume that the phenomena of life are possible only in their presence, that they are based upon chemical and physical changes of these constituents. The albumins are so prominent among these substances that some investigators have regarded them as the true basis of vital phenomena. Their great physiological importance has led chemists and physiologists to study their properties and reactions and to attempt to learn their chemical structure. Given a knowledge of their chemical structure, it would be possible to form an opinion in regard to the part played by them in the life processes.

In investigating albumins they have been subjected to hydrolysis and to oxidation. The first products of the breaking-down process are larger atomic groups—*albumoses, propeptones, peptones*. Further decomposition gives smaller atomic groups which are very stable towards some hydrolyzing agents. These latter products may be regarded as the building-stones of the albumin molecule.

There are certain albumins which, by gentle action of the decomposing agent used, break down into two parts, of which one is again an albumin, while the other is an organic or inorganic, but not albuminoid, atomic group. We must assume that in these cases the latter group is imposed upon an albumin molecule. The group thus split off from the albumin has been called a *prosthetic group*. The complex albumins that break down in this way into an albumin and a prosthetic group have been called *proteids* by Hoppe-Seyler. There is no doubt that many, if not most, of the atomic complexes that are active in the organisms are unstable compounds of albumin with other organic bodies.

When stronger chemical agents are allowed to act upon the albumin that is split off from the prosthetic group, another group of cleavage products is obtained. Lossen[2] oxidized egg albumin with potassium permanganate in the presence of magnesium sulphate and obtained guanidine. In 1890 Drechsel[3] studied the action of boiling baryta water on *lysatine*, a crystalline product formed by the action of aqueous

[1] Abstract of a lecture by A. Kossel, delivered before the German Chemical Society, June 1, 1901. See Ber. d. chem. Ges., 34, 3214.

[2] Ann. Chem. (Liebig), 201, 369 (1880).

[3] Archiv. f. Anatomie u. Physiologie, Physiol. Abth., 1891, p. 248.

hydrochloric acid on albumins, and obtained urea. This led him to believe that lysatine is the substance from which guanidine is formed in the oxidation of albumin. But Hedin showed that lysatine consists of *arginine* and *lysine*. E. Schulze and his pupils have shown that arginine, which occurs in nature in certain sprouts, yields urea and a compound of the formula $C_5H_{12}N_2O_2$ when treated with baryta water. When the compound $C_5H_{12}N_2O_2$ is treated with cyanamide, arginine is regenerated. The compound $C_5H_{12}N_2O_2$ turned out to be *ornithine*, a substance that had long been known as a product of animal metabolism. Ornithine has been shown to be 1,4-diamidovaleric acid. Quite recently E. Fischer[1] has succeeded in preparing a 1,4-diamidovaleric acid that is evidently the inactive form of ornithine. The relations between creatine, arginine, ornithine, and putrescine are represented by the following formulas :

$$
\begin{array}{llll}
& \diagup NH_2 & \diagup NH_2 & \\
C{=}NH & C{=}NH & & \\
\diagdown N{<}\!\!\begin{array}{l}CH_3\\CH_2\end{array} & \diagdown NH.CH_2 & CH_2.NH_2 & CH_2.NH_2 \\
\quad | & \quad\dot CH_2 & \quad\dot CH_2 & \quad\dot CH_2 \\
\quad COOH & \quad\dot CH_2 & \quad\dot CH_2 & \quad\dot CH_2 \\
& \quad\dot CH.NH_2 & \quad\dot CH.NH_2 & \quad\dot CH_2 \\
& \quad\dot COOH & \quad\dot COOH & \quad\dot CH_2.NH_2 \\
\end{array}
$$

| Creatine. | Arginine. | Ornithine. | Putrescine. |
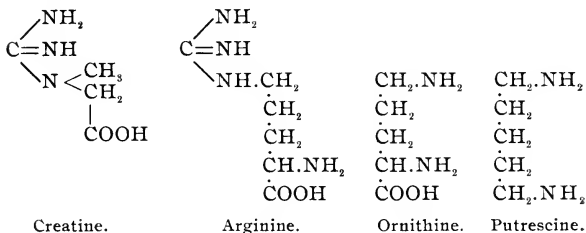
Lysine has been shown by Drechsel to be α,ε-diamido-caproic acid, and the same chemist has found diamidoacetic acid among the decomposition products of albumin. Finally, *histidine*, a substance of the formula $C_6H_9N_3O_2$, belongs to this same group of basic cleavage products of albumin.

The next group of cleavage products of albumin is that of the monamido acids. The simplest compound of this group is glycocoll, which is very frequently met with. The next member of the group of amido acids, *alanine*, or α-amidopropionic acid, has been found among the decomposition products of fibroïn from silk. But the derivatives of this acid, formed by oxidation, or by the introduction of sulphur, or by the addition of an aromatic group, are of greater importance than the acid itself. Among these are *serine* obtained from silk, and *cysteïne* obtained from *cystine*. The relations between these substances have been clearly established. They are represented by the following formulas :

[1] Ber. d. chem. Ges., **34**, 454 (1901).

$$
\begin{array}{ccc}
\text{CH}_3 & \text{CH}_3 & \text{CH}_3 \qquad \text{CH}_3 \\
| & | & | \qquad\quad | \\
\text{C} \overset{\text{NH}_2}{\underset{\text{OH}}{<}} & \text{C} \overset{\text{NH}_2}{\underset{\text{SH}}{<}} & \underset{|}{\text{C}} - \text{S} - \text{S} - \underset{|}{\text{C}} \\
| & | & \\
\text{COOH} & \text{COOH} & \text{COOH} \qquad \text{COOH} \\
\text{Serine.} & \text{Cysteïne.} & \text{Cystine.}
\end{array}
$$
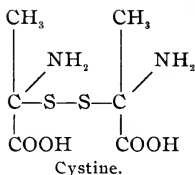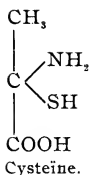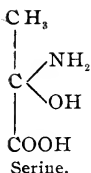
Recently, Mörner[1] has shown that when horn is treated with hydrochloric acid two cystines are formed, a laevorotatory and a dextrorotatory variety.

Other derivatives of amidopropionic acid that are obtained from albumin contain an aromatic nucleus. *Phenylalanine* (phenyl-α-amidopropionic acid) which was first found in sprouting plants, and later as a product of the cleavage of vegetable albumins, is one of these. Another is *tyrosine*, which was discovered by Liebig in 1848, and has since then been regarded as a characteristic cleavage product of albumins. Tyrosine is a laevorotatory p-hydroxyphenyl-α-amidopropionic acid. The relation between phenylalanine and tyrosine is shown by the formulas:

$$C_6H_5CH_2.CH(NH_2)COOH, \text{ Phenylalanine};$$

$$p\text{-}C_6H_4 \overset{OH}{\underset{CH_2.CH(NH_2)COOH}{<}}, \text{ Tyrosine.}$$
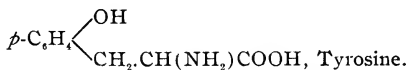
An amidobutyric acid and an amidovaleric acid have been found among the cleavage products of albumin, but *leucine*, which is the laevo rotatory α-amidoisobutylacetic acid, is much more commonly and abundantly met with, and together with this a compound, $C_{12}H_{22}N_2O_2$, called *leucineimide*. This is to be regarded as a derivative of diacipiperazine formed by the combination of two molecules of leucine:

$$
\begin{array}{cc}
\text{CH}_3 \quad \text{CH}_3 & \text{C}_4\text{H}_9 \\
\diagdown \quad \diagup & | \\
\text{CH} & \text{CH} \\
| & \diagup \quad \diagdown \\
\text{CH}_2 & \text{NH} \qquad \text{CO} \\
| & | \qquad\quad\quad | \\
\text{CH.NH}_2 & \text{CO} \qquad \text{NH} \\
| & \diagdown \quad \diagup \\
\text{COOH} & \text{CH} \\
& | \\
& \text{C}_4\text{H}_9
\end{array}
$$
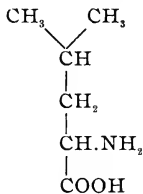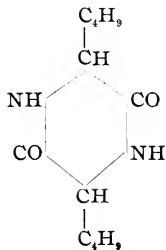
Leucine.   Leucineimide.

[1] Ztschr. physiol. Chem., **28**, 595.

Emil Fischer has recently found active pyrrolidine-α-carbonic acid among the decomposition products of caseïn :

$$\text{H}_2\text{C} \overset{\displaystyle \text{NH}}{\diagup \diagdown} \text{CH.COOH}$$

$$\text{H}_2\text{C} \text{---} \text{CH}_2$$

Pyrrolidine-a-carbonic acid.
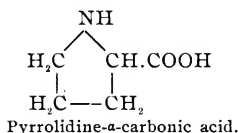
To the above-named amido acids and their derivatives, must be added aspartic acid, $COOH.CH_2.CH(NH_2).COOH$, and glutamic acid, $COOH.CH_2.CH_2.CH(NH_2).COOH$, as among the cleavage products of albumin.

Carbohydrates have repeatedly been obtained as prosthetic groups. That carbohydrate residues occur in the molecules of albumin appears probable from evidence furnished by investigations of Udransky.[1] This chemist has shown that when pure albumins are distilled with sulphuric acid furfurol is obtained. The formation of furfurol was regarded by him as evidence of the presence of a carbohydrate group in albumins. The cause of the formation of the furfurol has, however, not yet been determined.

When other chemical agents besides dilute acids or alkalies, such as enzymes, oxidizers, fusing alkalies, are used for the purpose of breaking down the albumin molecule, products are obtained that are essentially the same as those already mentioned, or they are such as can be formed by further transformation of these. Thus, the fatty acids that are formed when albumins are treated with fusing potassium hydroxide have their origin in the amido acids ; paraoxybenzoic acid comes from tyrosine ; and benzoic acid from that constituent of albumin that yields phenylalanine.

It is evident that all the atomic groups contained in the albumin molecule cannot be detected by hydrolysis by means of acids and alkalies. More energetic hydrolysis destroys that group which gives the biuret reaction—a red coloration caused by copper sulphate in the presence of caustic soda. The first decomposition products, which are similar to the original albumins, give this reaction very strongly. By further action of the hydrolyzing agent the reaction disappears, and we can therefore distinguish between products that give the biuret reaction and products that do not give the biuret reaction.

Just as the biuret-forming group disappears, so also one aromatic group of the albumin molecule disappears under the

[1] Ztschr. physiol. Chem., **12**, 389.

influence of dilute acids. When bromine acts upon albumins in the presence of water, tribromamidobenzoic acid is formed. Neither of the two aromatic groups which are obtained by simple hydrolysis contains an amido group in the benzene ring, and we must therefore assume, either (1) that, besides the tyrosine and the phenylalanine, a third aromatic group exists, or (2) that an atomic rearrangement takes place in these reactions. The first explanation is in harmony with the formation of indol and skatol. When fusing alkali acts upon albumins, or they are subjected to the action of microorganisms, indolcarbonic acid and skatolcarbonic acid are formed. Under some circumstances skatolacetic acid, besides paraoxyphenylacetic and phenylacetic acids, can be obtained in the decomposition of albumin :

$$C_6H_4 \begin{cases} OH \\ CH_2.COOH \end{cases}, \text{ Paraoxyphenylacetic acid ;}$$

$$C_6H_5CH_2.COOH, \text{ Phenylacetic acid ;}$$

$$C_6H_4 \begin{cases} CCH_3 \\ C.CH_2COOH \\ NH \end{cases}, \text{ Skatolacetic acid.}$$
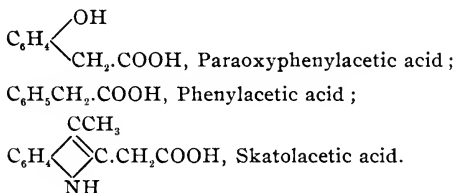
Nencki regards these three compounds as representatives of the three forms in which the benzene group is contained in the molecule of albumin.

The decomposition-products of albumin, according to the above, may be brought under four heads :

1. The urea-forming group to which arginine belongs.

2. The group of the diamido acids. Diamidovaleric acid is combined with the urea-forming group in arginine.

3. The group of the monoamido acids.

4. Finally, other products are obtained, the relations of which to the above groups are not yet known.

On the other hand, the number of albumins is very large. These can be distinguished between by differences in solubility, in their conduct towards precipitating reagents, and by other peculiarities. Every typical albumin of animal or vegetable origin gives most of the above-named groups. The molecule of albumin must therefore be of extraordinary complexity. The investigation of the structure of albumin would be extremely difficult even if the individuality and purity of the albumins were beyond all doubt. But this is far from being the case. And further, the albumins combine with

other substances with the greatest ease. Of special importance is the fact that they combine with one another. This makes it appear probable that most of the albumins that have been isolated from animal tissues are complex compounds of several simpler albumins. A number of facts go to show that when the large molecule of albumin is broken down by hydrolysis, oxidation, or the action of enzymes, it yields (1) several smaller molecules (*albumoses*) which then break down into (2) still smaller biuret-forming atomic complexes (*peptones* in the modern sense), and finally into (3) the above-named products that do not give the biuret reaction.

Owing to the great difficulties encountered in the investigation of typical complex albumins, the author has tried to get light on the problem by seeking in nature for simpler albumins. Such substances are the protamines that are found in the spermatozoa of fish. The first member of this class was discovered thirty years ago by Miescher in the spermatozoa of the salmon. He described it as a substance of the formula $C_9H_{21}N_5O_3$, Kossel[1] later found basic compounds in the spermatozoa of other fishes. These resemble the protamine of the salmon or *salmine*, but are not identical with it. Such are *sturine* from the testicles of the sturgeon,[2] and *clupeine* from the testicles of the herring.[3]

The protamines are compounds of strong basic properties. They have a high molecular weight—at least the free bases do not raise the boiling-point of water. Hydrolysis has shown that there are several groups of these protamines. The simplest, salmine and clupeine, break down into arginine, amidovaleric acid, and a residue, the nature of which is not yet known. The quantity of arginine obtained from salmine is 84.3 per cent, from clupeine it is 82.9 per cent of the protamine taken. According to this, 87.8 per cent of the total nitrogen in salmine, and 83.5 per cent of that in clupeine, is in the form of arginine.

Each of the three protamines above named therefore contains three of the characteristic groups of the albumins—the urea-forming complex, diamidovaleric acid, and amidovaleric acid. That these groups are arranged in the protamines in a way similar to that in which they are arranged in the complex albumins appears probable from the fact that the protamines show the biuret reaction. The propeptones and peptones, as has been pointed out, are intermediate products that are

[1] Verhandl. d. naturforsch. Gesell. in Basel, VI., Heft 1, ss. 138–208 ; Picard : Ber. d. chem. Ges., **7**, 1714 (1874).

[2] Ztschr. physiol. Chem., **22**, 176.

[3] *Ibid.*, **25**, 165.

formed when the original albumins are broken down into the abiuretic substances (substances that do not give the biuret reaction). Similar intermediate products are formed from protamines. These are called *protones*. The protamines, like the typical albumins, have colloidal properties, and they can easily be salted out. As they pass over into the protones these properties are gradually lost, as is the case in the peptonization of the albumins.

In all attempts to bring the group of albumins into a chemical system the fact must be kept in mind that the molecule of albumin is composed of several like or unlike parts, the albumoses or peptones, a knowledge of which must be the first object of the investigation. In order to get a general conception of the constitution of the albumin molecule, it will be desirable to fix our attention upon some one group contained in the albumins, and to regard the albumoses and peptones as formed by the addition of different groups to this *nucleus*. We must, of course, for this purpose, select as this nucleus a group that is contained in all albumins or in as many as possible—even in the protamines. Arginine answers these conditions best. In this light, the simplest biuret-forming complexes, the protones and the protamines, are to be regarded as formed by the addition of a monamido acid, amidovaleric acid, and of another substance still unknown to the arginine group. In the case of the higher protamines there is, of course, greater complexity of the molecule.

The differences in the relative quantities of the various groups that go to make up the albumin molecule would suffice to explain the existence of a large number of albumins. Possibly other differences may be due to the arrangement of the constituent groups in space. At all events, it is clear that the conception of "albumin" as a factor of constant value, as always signifying the same thing, is unjustifiable.

It has been pointed out that, in the tissues and secretions of animals and plants, the albumins frequently occur in combination with other groups. The physical properties of these *proteids* are essentially those of the albumins, and hydrolysis is generally necessary to determine whether these substances consist of two constituents, an albumin, or at least a biuret-forming compound (peptone), and the prosthetic group.

The union of the albuminous constituent and the prosthetic group may be more or less firm. Hoppe-Seyler,[1] for example, has shown that in the yolk of eggs lecithine is combined with albumin very loosely, the compound being broken down even by hot alcohol. In other cases energetic action is required to

[1] "Physiologische Chemie," Berlin, 1877-81, p. 781.

effect this separation of the prosthetic group from the albumin.

In a few cases it has been possible not only to decompose the proteid into its constituents, but also to cause these constituents to combine to form the proteid. Altman,[1] for example, has shown that the prosthetic group of many nucleins, *nucleic acid*, gives with albumin a precipitate that has the properties of the original proteid, nuclein.

The prosthetic groups are of many kinds. An inorganic group, a phosphoric acid, for example, may combine with the biuret-forming complex ; in other cases a complicated organic group may be united with the albumin.

The glycoproteids have of late attracted the attention of physiological chemists. These are made up of a carbohydrate group combined with albumin, and investigations are now in progress involving these substances.

In the so-called nucleins the carbohydrate complex appears to be united with a large number of other atomic groups. In the nucleic acids at present known, different carbohydrates are undoubtedly contained. The other groups thus far found in the nucleic acids belong essentially to the pyrimidine group. The investigations of the last twenty years have shown that the derivatives of pyrimidines play a very important part in the fundamental vital phenomena. Kossel has found them in the place where the synthetical processes—the phenomena of growth—take place, that is to say, in the cell nucleus.

I. R.

The Dissociating Power of Liquid Hydrocyanic Acid.

A paper has just appeared by Centnerzwer[2] describing an investigation on the dissociating power of liquid hydrocyanic acid. This investigation was carried out under the guidance of Prof. Walden, whose work on non-aqueous solvents is so well known. After showing that liquid cyanogen has practically no dissociating power, it seemed desirable to study, in this connection, liquid hydrocyanic acid, and especially for the following reasons :

First : The nitriles CH_3CN, C_2H_5CN, etc., have strong dissociating power.

Second : In homologous series such as HOH, CH_3OH, C_2H_5OH, or HNH_2, CH_3NH_2, $C_2H_5NH_2$, the first member has much the strongest dissociating power.

Third : Hydrocyanic acid being the first member of the

[1] Archiv. für. Anat. u. Physiolgie (physiol. Abtheilung), 1889, p. 524.

[2] Ztschr. phys. Chem., **39**, 217.

homologous series of nitriles should have especially strong dissociating power.

Fourth : Liquid hydrocyanic acid has been shown to have a very high dielectric constant, 95, while that of water, at the same temperature, is only about 80. From the relation pointed out by J. J. Thomson, and later by Nernst, between the dissociating power of a solvent and its dielectric constant, hydrocyanic acid should have a very high dissociating power.

The method employed in measuring the conductivity of the solutions is very simple. The apparatus is shown in the accompanying sketch :
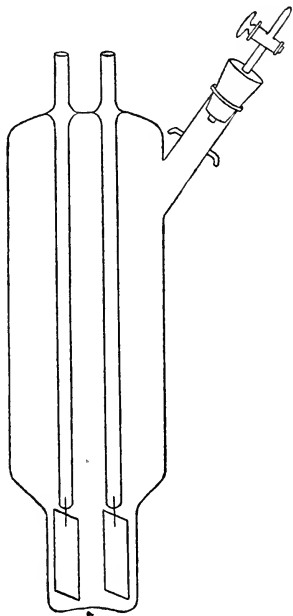
A fairly concentrated solution of the salt in the solvent was prepared by bringing the two together in weighed quantities. This solution was introduced into the vessel and its conduc-

tivity determined. A part of the solution was then poured out through the stop-cock, and replaced by the pure solvent. The conductivity of the new solution was then determined and this process repeated until the most dilute solution was reached.

The conductivity of the solvent was found to vary somewhat, the purest specimen having the value 0.496×10^{-5} in reciprocal Siemens' units.

The conductivities of potassium iodide and trimethyl sulphonium iodide, in liquid hydrocyanic acid, were determined. The molecular conductivities at the different dilutions, together with the molecular conductivities of these same substances in water, are given below :

Molecular Conductivities of KI at Zero.

In liquid HCN.		In H_2O.	
$v.$	$\mu_v.$	$v.$	$\mu_v.$
8	241	25.3	73.1
16	248	50.6	79.0
32	255	75.9	81.9
64	262		
128	268		
256	276		
512	282		
1024	289		

Molecular Conductivities of $S(CH_3)_3I$ at Zero.

In liquid HCN.		In H_2O.	
$v.$	$\mu_v.$	$v.$	$\mu_v.$
16	259	32	70.9
32	274	64	74.4
64	285	128	78.5
128	294	256	79.9
256	300		
512	307		
1024	311		

It is obvious from the above results that the conductivity of these substances in liquid hydrocyanic acid is several times greater than that in water at the same dilutions, and it is very probable that the dissociating power of this solvent is even greater than that of water. Before this conclusion could be accepted as final, the values of μ_∞ for the salts in hydrocyanic acid must be accurately determined. This conclusion, however, is made probable by the fact that the molecular conductivity increases very slowly with increase in dilution for the more

dilute solutions studied, indicating that the value of μ_∞ had been very nearly reached in the most dilute solutions used. Centnerzwer concludes his paper with the observation that the dissociating power of this solvent, "together with the high value of its dielectric constant, furnishes a new confirmation of the Thomson-Nernst law of parallelism between dissociating power and dielectric constants."

This investigation is of special interest in that it makes it very probable that a solvent has been found which has a greater dissociating power than water. A number of attempts have been made to find such a solvent, and while it is possible that hydrogen dioxide may be a stronger dissociant than water, this is far from proved.

That this solvent conforms to the Thomson-Nernst hypothesis is also of interest, but it should be noted that while this hypothesis accords very beautifully with the theory of electrolytic dissociation, it is not a necessary consequence of the theory. If solvents, therefore, did not conform to the hypothesis it would not affect, in the slightest, the validity of the theory of electrolytic dissociation.   HARRY C. JONES.

REVIEWS.

A LABORATORY GUIDE TO THE STUDY OF QUALITATIVE ANALYSIS. By E. H. S. BAILEY, PH.D., Professor of Chemistry, and HAMILTON P. CADY, A.B., Assistant Professor of Chemistry in the University of Kansas. Fourth edition. Philadelphia : P. Blakiston's Son & Co. 1901. pp. 234.

The object which the authors had in mind in preparing this work can be clearly seen by quoting a paragraph from their preface : "At the present time there seems to be an opportunity to broaden the methods of instruction in Qualitative Analytical Chemistry, and to teach not only the facts and the mechanical methods of carrying out the various operations of analysis, but also to render them more intelligible and interesting to the student, by a proper application of the theory of Electrolytic Dissociation and of the Mass Law. In the past we have had to be content with a bare statement of facts, which were largely unrelated, but the dissociation theory of Arrhenius and the law of mass action, as enunciated by Guldberg and Waage, have furnished us with a means of correlating and interpreting chemical phenomena."

The aim of this work is undoubtedly in the right direction. The theory of electrolytic dissociation, the law of mass action, the phase rule, and similar epoch-making generaliza-

tions have been frequently regarded as important in physical chemistry, but it has been held by many that it would be impossible, or at least undesirable, to introduce them into elementary courses in inorganic chemistry. In the last year or two a great change has been experienced. In 1900 the "Grundlinien der anorganischen Chemie" by Ostwald appeared, which showed how certain physical chemical conceptions can and ought to be introduced into general chemistry; and in the same year the "Lehrbuch der anorganischen Chemie," by Holleman, was published. The work of Holleman goes farther in certain directions than that of Ostwald, and, together with the latter, marks a new epoch in the development of inorganic chemistry.

That the principles which lie at the foundation of these works are finding practical application in the laboratory is shown by the appearance of a manual like the one in hand. Perhaps a little different treatment of certain subjects and a little fuller treatment of others would have been advantageous, but these are minor points. This book will undoubtedly contribute its share towards the application of physical chemical generalizations to inorganic chemistry.

The book is only about half the size that would be indicated by the number of pages, since half the pages are left blank for students' notes.   H. C. J.

THE PRACTICAL METHODS OF ORGANIC CHEMISTRY. By LUDWIG GATTERMANN, PH.D., Professor in the University of Freiburg. Translated by WILLIAM B. SCHOBER, PH.D., Instructor in Organic Chemistry in Lehigh University. The second American from the fourth German edition. New York: The Macmillan Co. 1900.

The first edition of this book was reviewed in this JOURNAL,[1] and attention was called to its excellence as a laboratory guide, combining as it does not only a very exact and thorough treatment of the details of the preparation of typical substances, but also in each case calling attention to the general principles involved and the general reactions of the substances, and the bearing of each case on others. In this edition a number of new preparations have been introduced, some of which have been devised since the last edition was published. The preparation of acetylene and acetylene tetrabromide have been omitted in this edition, no doubt owing to the fact that calcium carbide is now so accessible for the preparation of acetylene. This book should be in the hands of all who are teaching organic chemistry or are making or-

[1] This JOURNAL, **19**, 79.

ganic preparations, as it is thoroughly up to date and more comprehensive and thorough than some of the books used for this purpose.   J. E. G.

LEHRBUCH DER ANORGANISCHEN CHEMIE, FÜR STUDIERENDE AN UNIVERSITÄTEN UND TECHNISCHEN HOCHSCHULEN. Von DR. A. F. HOLLEMAN, o. Professor der Chemie an der Universität Groningen, in Gemeinschaft mit dem Verfasser bearbeitet und herausgegeben von DR. PHIL. WILHELM MANCHOT, Privatdocent der Chemie an der Universität Göttingen. Mit zahlreichen Abbildungen und zwei Tafeln. Verlag von Veit und Comp., Leipzig. 1900. pp. 439.

Less than two years ago the " Grundlinien der anorganischen Chemie," by Ostwald, appeared. This showed for the first time how physical-chemical generalizations can be applied to inorganic chemistry, and can, indeed, be made the basis of this branch of chemical science. In the same year the work in hand was published, which goes farther in certain directions than that of Ostwald. The way in which this book differs from the earlier works on inorganic chemistry can be seen best by reference to certain paragraphs.

After a consideration of ozone and hydrogen dioxide, the determination of molecular weights by the freezing-point and boiling-point methods is taken up. Having discussed hydriodic acid, the question of dissociation by heat is considered. In this connection the subjects of equilibrium in reactions in general and the order of reactions are entered into, and the equations both for first and second order reactions are developed. The theory of electrolytic dissociation is introduced after a number of the halogen acids have been studied. The phase rule is taken up in connection with sulphur, which furnishes such an excellent example of one substance existing in four phases. On page 136, after sulphur, selenium and tellurium, a chapter is devoted to thermochemistry and thermodynamics as applied to chemistry. Very much later in the work, after zinc, cadmium, and mercury have been taken up, a short chapter is devoted to electrochemistry, including a calculation of the electromotive force of primary cells, a discussion of the storage battery, the Leclanché element, etc.

It is obvious from the above that we have here also a departure from the text-books already existing in inorganic chemistry. Many of the fundamental conceptions of physical chemistry are introduced and applied to the phenomena of inorganic chemistry.

After a careful study of the book, the question may, however, be raised, Are these generalizations always introduced naturally into the subject, or are they forced in at certain places? In a few cases it must be confessed that they do not

seem to fall naturally into the contents of the work, and in other cases it is a question whether these physical-chemical ideas have not been carried a little too far. Take the chapter on thermodynamics as applied to chemistry. This is so far above the level of the average reader of a book on inorganic chemistry that it will make but little impression upon him. But even here the question arises whether everything in a book should be written on the level of the average reader, or should the reader be required to make some effort to overcome difficulties which at first sight seem insurmountable?

These are, however, minor points. The main object of the work is excellent. It aims to introduce simple mathematical generalizations into inorganic chemistry, which is the first step toward placing chemistry upon the basis of an exact science. It is universally recognized that chemistry is much less fully developed than physics, and this has been attributed chiefly to the nature of chemical phenomena. These, as a whole, are more complex than physical phenomena, and, further, chemical reactions frequently proceed in steps, one part of A combining with one, two, three parts of B. Both of these influences have made it far more difficult to deal with the phenomena of chemistry by the only exact method, *viz.*, the mathematical.

It is one of the crowning glories of physical chemistry that these difficulties have been, at least in part, overcome, and many of the phenomena which twenty years ago were necessarily treated as empirical facts, can now be dealt with by rigid methods, and their meaning and significance seen.

The book in hand, together with Ostwald's '' Grundlinien,'' undoubtedly marks a new epoch in the development of the science of inorganic chemistry.   H. C. J.

AMERICAN

CHEMICAL JOURNAL

ON THE FORMATION, DECOMPOSITION AND GERMICIDAL ACTION OF BENZOYL ACETYL AND DIACETYL PEROXIDES.

BY PAUL C. FREER AND FREDERICK G. NOVY.

Hoitsema[1] has shown that the amount of hydrogen dissolved in palladium is, within certain limits, directly proportional to the pressures exerted, but if these are very small, then the quantity is proportional to the square root. The conclusion to be reached is, therefore, that, under these conditions, the hydrogen is present in the form of individual atoms. The formation of water from hydrogen and oxygen, under ordinary conditions, takes place with unmeasurable slowness, but is increased to measurable rapidity by the presence of certain substances, so that with finely divided metals, such as platinum or palladium sponge, the rate of change is often so rapid that explosion may occur. Unquestionably, in these cases, the metal has a specific action, but the intensity of this is increased by increasing the surface. The gases in these cases are, perhaps, best considered as being in solution in the solids, and the dissociating action of solvents would produce

[1] Ztschr. physik. Chem., 17, 1.

11-27

the monatomic condition made apparent by Hoitsema.   Mond, Ramsay, and Shields[1] have shown that palladium foil, sponge, or black take up equal quantities of hydrogen, so that the solubility of the gas is independent of the surface.   The hydrogen in these solutions has the characteristics of a metal, and observing the analogy between this and fluid solutions of one metal in another, it also seems probable that the hydrogen is in the form of individual atoms.   The increased activity can be explained not only by the greater concentration of hydrogen in unit space, but also by the dissociation which has taken place.   The resistance to the oxidation of gaseous hydrogen may rest upon the slow rate at which the molecules are split into atoms, and this dissociation takes place more rapidly in metallic solution, thus accounting for the increased rate of oxidation.   The same must be true, to a greater or less extent, of all surfaces, although not all have the same solvent or dissociating power for hydrogen.

In the case of oxygen there is no such marked absorption by metals, so that instances in which oxygen is undoubtedly rendered active by the presence of catalyzers are not frequent. The change from sulphur dioxide to sulphur trioxide by the action of platinized asbestos or platinum is unquestionably an example.[2]   The oxidation of mixtures of benzaldehyde and acetic anhydride, when spread on sand and exposed to the air, produces, according to the conditions, either benzoyl peroxide[3] or benzoyl acetyl peroxide.[4]   These reactions were, in our opinion, also cases in which the catalytic action of the solid surface brought about the oxidation, so that, while undertaking some bacteriological studies on the action of organic peroxides, we also studied the influence of catalytic agents on the formation of this class of bodies.

Nef has shown that the formation of benzoyl acetyl peroxide (accompanied by that of benzoyl acetyl oxide and benzoic acid), is much more rapid when the mixture of benzaldehyde and acetic anhydride is spread upon sand than when it is exposed to the air in glass vessels; this acceleration, in his

[1] Proc. Roy. Soc., **62,** 290.

[2] For an extended review of this subject see Bodländer's Ahrens Vorträge, **3,** 385.

[3] H. Erlenmeyer, Jr. : Ber. d. chem. Ges., **27,** 1959.

[4] Nef : Ann. Chem. (Liebig), **298,** 280.

paper, is tacitly ascribed simply to mechanical causes, owing to the greater ease of contact between the air and the mixture. In order to determine whether the contact of a sufficient volume of air is alone necessary for rapid peroxide formation, or whether the surface action of a solid is necessary, we performed the following experiments:

Fifty grams of benzaldehyde and 50 grams of refractioned acetic anhydride were placed in an ordinary gas washing-bottle, the entrance tube of which was drawn out to a number of capillaries, so as to insure a very fine division of the air bubbles. This wash-bottle was placed in a freezing-mixture and air, previously cooled by passing th rough a worm and drying bottle with concentrated sulphuric acid, both packed in a freezing mixture, was passed through in a rapid stream for seven hours, at the end of which time the contents of the bottle suddenly solidified. The crystals were separated and recrystallized from petroleum ether, when they proved themselves to be pure benzylidene diacetate. The yield was only a little less than quantitative, and only minimal quantities of either benzoyl acetyl peroxide or benzoic acid were formed. Repetition of the experiment, at the same temperature, produced the same result. At higher temperatures (13° to 14°), even after a current of air had freely passed for twenty-four hours, only a trace of peroxide was produced, but at the same time no benzylidene diacetate, or at least no quantities sufficient for isolation from the mixture in the flask, could be observed. The benzaldehyde and acetic anhydride were almost completely unchanged. The rapid formation of benzylidene diacetate, therefore, seemed to be dependent upon the condition of low temperature. The result shows that, when the mixture of benzaldehyde and acetic anhydride is kept agitated by a rapid current of nearly dry air, the formation of benzylidene diacetate is much more rapid than when the mixture is left standing alone, for Nef[1] found only 2 grams of benzylidene diacetate formed from 48 grams of benzaldehyde, even after five days' standing. In Nef's experiments a large quantity of acetic acid (24 grams) was added, whereas in the above, the acetic anhydride was twice refractioned, and so could contain

[1] Ann. Chem. (Liebig), **298**, 278.

only a trace of acetic acid.   A large quantity of acetic acid,
therefore, has no influence in increasing the rate of action,
but on the contrary it seems to diminish it.   If Nef's assump-
tion that the formation of benzylidene diacetate is due to a
previous addition of acetic acid, separation of the latter to
form nascent benzaldehyde, and subsequent addition of acetic
anhydride, is correct :

$$
\begin{array}{ccc}
\underset{H}{\overset{C_6H_5}{\diagdown}} C \underset{OCOCH_3}{\overset{OH}{\diagup}} & \longrightarrow & \underset{H}{\overset{C_6H_5}{\diagdown}} C - O \; ; \\
\end{array}
$$

$$
\underset{H}{\overset{C_6H_5}{\diagdown}} C - O + O \underset{COCH_3}{\overset{COCH_3}{\diagup}} = \underset{H}{\overset{C_6H_5}{\diagdown}} C \underset{OCOCH_3}{\overset{OCOCH_3}{\diagup}} .
$$
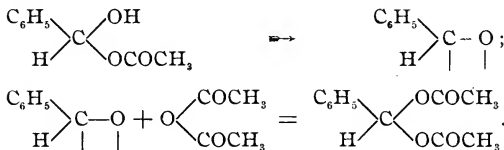
Then the increase in the concentration of the acetic acid should
accelerate rather than retard the rate of reaction.

In order to test whether substances other than acetic acid
would also affect the rate of formation of benzylidene diace-
tate, 10 grams of aldehyde and 10 grams of refractioned
acetic anhydride were placed in a tube with a strip of platinum
foil, 1 cm. wide and 5 cm. long, and dry air was run through
for twenty hours.   The current was very slow, so as to secure
merely an agitation of the liquid.   At the end of this time
16.5 grams of benzylidene diacetate had been formed ; calcu-
lated 19.5 grams.   By far the greater portion of this diacetate
was produced in the first hour, and the tube at the beginning
became quite warm, showing that under these conditions the
addition of acetic anhydride to benzaldehyde is much accelera-
ted, although only a trace of acetic acid could be present.
On repeating the above experiment, all conditions being the
same except that the tube was cooled to 10°, the formation of
the diacetate was retarded so that the change was not com-
plete for three days.   The same mixture, sealed in a tube and
placed in the shaking machine, solidified completely, forming
benzylidene diacetate after seven hours, so that agitation by
means of a current of air did not accelerate the reaction.
Other metals have even a more marked effect.   Zinc and tin,
when placed in tubes containing the mixture of aldehyde and
anhydride, effect the change in about half an hour, with a

slow current of air passing through, and with iron the reaction-products become heated at once, and the addition is complete after a few minutes.

Various metals, therefore, exert a marked catalytic action on the formation of benzylidene diacetate, independently of the amount of acetic acid which may be present. Acetic acid, however, may act as a catalytic agent, increasing the velocity of the reaction, but not altering the final equilibrium. Indeed, in accordance with Nef's results, we have found that acetic anhydride which had been freed from acetic acid by standing over sodium and then distilling, did not form benzylidene diacetate in appreciable quantities, with iron and a slow current of air, until thirty-six hours had elapsed. And probably, as in Nef's case, mixtures of benzaldehyde and acetic anhydride, purified in this manner, if simply standing in a closed flask, would react with such extreme slowness that amounts of benzylidene diacetate sufficient for isolation would not be produced for months. We have not completed our work on the action of catalysis in the formation of benzylidene diacetate, as very slight variations in the purity of the materials or of the catalyzers produce such marked variations in the rate of formation that concordant results are difficult to obtain. Neither have we determined whether a mixture of benzaldehyde and acetic anhydride, purified by standing over sodium, will eventually produce benzylidene diacetate, but the work has gone far enough to demonstrate that various substances have different effects on the rate of addition, and that even traces of acetic acid are just as effective as the large amounts used by Nef.

The conclusion, therefore, is that the action of acetic anhydride on benzaldehyde is purely one of addition, and that the course of the reaction is simpler than the one proposed by Nef. It is nevertheless probable, in view of the work of Baeyer and Villiger[1] on benzoperacid and on the oxidation of benzaldehyde, as well as the other additive reactions in which benzaldehyde takes part, that a methylene derivative,

$$\begin{array}{c} C_6H_5 \\ \diagdown \\ H-O \diagup \end{array} C \diagup \;,$$
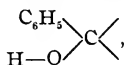
[1] Ber. d. chem. Ges., **33**, 1582.

takes part in the reaction. Many changes which aldehydes undergo can best be explained by the existence of an equilibrium between the two isomers

$$\text{I.} \quad \underset{H}{\overset{R}{>}}C=O \qquad \text{and} \qquad \text{II.} \quad \underset{H-O}{\overset{R}{>}}C<.$$
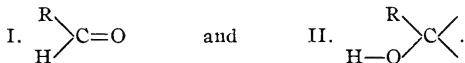
Only a trace of the enol form (II.) need be present to start reactions. As soon as form II. is removed, the equilibrium is restored by a renewed change from I. (keto form) to II. (enol form), and so on until reaction is complete. The ease with which the change can be brought about would determine the rate at which a given aldehyde would react. The existence of an equilibrium between keto and enol form in acetoacetic ether is now extremely probable, in view of the work of Schiff,[1] as well as the large mass of modern literature on desmotropic forms of substances, which seems to show that an equilibrium between the two forms exists in many liquid aldehydes and ketones. This view need only be extended to ordinary aldehydes of the form $\underset{H}{\overset{R}{>}}C=O$ to have a rational explanation of the various reactions of this class of bodies. Catalyzers, as in the above case of the formation of benzylidene diacetate, would then simply affect the rate of change of keto to enol form, on exactly the same principle as we suppose that catalyzers can increase the rate of dissociation of the hydrogen molecules into atoms in the formation of water.[2] The relative inactivity of the carbonyl oxygen atom in the carboxyl group

$$\underset{H-O}{\overset{R}{>}}C{\overset{O}{<}} \quad \longrightarrow \quad \underset{O}{\overset{R}{>}}C{\overset{OH}{<}} \qquad \textit{versus}$$

$$\underset{H}{\overset{R}{>}}C{\overset{O}{<}} \quad \longrightarrow \quad \underset{H-O}{\overset{R}{>}}C<,$$
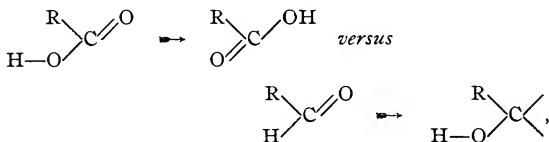
would thus be explained by the mere fact that two distinct forms, one of which is the intensely reactive unsaturated form, and the consequent equilibrium are not possible, and

[1] Ber. d. chem. Ges., **31**, 205, and following.
[2] Bodländer : Ueber langsame Verbrennung, Ahrens Vorträge, **3**, 439.

hence carbonyl in the carboxyl group cannot behave like carbonyl in aldehydes and ketones.

As the rapid formation of benzylidene diacetate, provided acetic anhydride, which has merely been refractioned, is used, causes the contents of the tubes through which air is passed to solidify before appreciable quantities of peroxide are formed, we were compelled, in all experiments relating to the influence of surface on the rate of oxidation, to use acetic anhydride which had stood over sodium for some time, and which was then poured off and refractioned. By this means the formation of benzylidene diacetate is so greatly retarded that, in most cases, we were able to run air through the mixture of benzaldehyde and acetic anhydride long enough to obtain quantities of benzoyl acetyl peroxide which could be quantitatively determined.

The problem of ascertaining the amount of peroxide which is present in a mixture of benzaldehyde, acetic anhydride, acetic acid, benzylidene diacetate, and benzoyl acetyl oxide, all of which bodies must be present in the reacting liquid after air has been run in for a sufficient length of time, is not an easy one, and we soon discovered that such means as decolorizing indigo or titration with potassium iodide could not give accurate results. We finally adopted the method of heating a measured quantity of the mixture resulting from oxidizing benzaldehyde and acetic anhydride by means of a current of air and measuring the evolved gas. That this gives a reasonably accurate means of quantitatively determining benzoyl acetyl peroxide in the presence of all of the other substances occurring during the reaction is shown by the following experiments :

A weighed quantity of benzoyl acetyl peroxide was dissolved in about 5 cc. of benzaldehyde and the solution placed in a small, round-bottomed flask, which was connected with a carbon dioxide apparatus on the one side and a Schiff's azotometer on the other. After all air had been expelled the flask was heated with a free flame until evolution of gas began, then the flame was removed, and only brought under the flask from time to time, as the reaction required. The decomposition must take place as rapidly as possible, without causing explosion.

Gram peroxide used.	Calculated gas volume for 1 molecule gas per 2 molecules peroxide.	Found.
0.2445	15.1	14.3
0.1199	7.4	7.3
0.2084	12.9	12.7
0.2018	12.5	12.3
0.0941	5.8	6.0
0.3306	20.5	21.2

As will be seen from the above, 1 molecule of gas is developed for every 2 molecules of peroxide, and the method is sufficiently accurate for all purposes of measurement. No gas whatever is obtained on heating pure benzaldehyde or a mixture of benzaldehyde and acetic anhydride, or any other mixture not containing peroxide under the above conditions, as we have proved to our satisfaction. The gas collected over potash, much to our surprise, proved to be methane.

The gas collected from 5 grams of benzoyl acetyl peroxide was allowed to stand over strong potash solution for twenty-four hours and was then analyzed by combustion.

	Calculated for CH_4.	Found.
C	75.0	75.4
H	25.0	24.6

A gas analysis, kindly carried out by Mr. White, of this laboratory, by the usual methods, confirmed the combustion and proved the gas to be methane. The gas does not reduce a solution of palladium chloride, hence no hydrogen is present.

If the gas given off by heating benzoyl acetyl peroxide is collected over mercury, then the volume is equal to that calculated for 4 molecules of gas for every 2 molecules of peroxide decomposed, and of these four molecules three are carbon dioxide.

I. 1.111 grams substance in 40 cc. of xylene were decomposed by heating to 105° in an oil-bath, the temperature being gradually increased to 155°, and the total gas collected over mercury. The gas was then passed through a potash bulb by means of a current of air, free from carbon dioxide, and the carbon dioxide weighed. Found 0.379 gram CO_2.

II. 1.238 grams substance in 20 cc. of xylene were decom-

posed as above, care being taken not to heat above 110°.
Found 0.431 gram CO_2.

	Calculated for 3 mole-cules CO_2 to 2 mole-cules peroxide.	Found.	
		I.	II.
CO_2	36.8	34.1	34.8

The percentage of gas obtained is slightly low, but the de-composition is almost quantitative. A very minute quantity of benzoyl acetyl peroxide, therefore, decomposes differently. The volume of methane obtained also varies slightly from the calculated. The volume of gas not absorbable by potash varies somewhat if the peroxide is very slowly decomposed in xylene, but is fairly constant, as shown above, if the sub-stance is heated over a free flame.

Two molecules of benzoyl acetyl peroxide, therefore, de-compose into 3 molecules of carbon dioxide, 1 of methane, and a liquid residue. The empirical equation would be :

$$2C_9H_8O_4 = 3CO_2 + CH_4 + C_{14}H_{12}O_2.$$
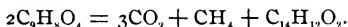
The high-boiling residue was examined as follows : The xylene was distilled under diminished pressure from the resi-due obtained by heating 5 grams. The remainder was then taken up in ether and extracted with sodium carbonate. On acidifying the carbonate, 0.11 gram of an acid was isolated. This acid has not been identified. The ether was then dis-tilled off and the non-acid remainder boiled for six hours on a water-bath with 2 grams of alcoholic potash. The alcohol was then distilled off and the whole taken up in water. The non-saponifiable portion was carefully extracted with ether. The alkaline solution, when acidified, gave 0.7 gram of ben-zoic acid. The non-saponifiable portion was fractioned at 18 mm. pressure. Two grams went over between 160° and 185°, and about an equal weight of high-boiling residue, which would not distil up to 265°, remained. The distillate is colorless and boils between 260° and 285° at ordinary pres-sure. It cannot be crystallized. No constant-boiling prod-uct could be obtained from it. An analysis showed this re-mainder to be a mixture of high-boiling hydrocarbons.

Weight of substance 0.1332.

		Found.	
	Gram.		Per cent.
H	0.0114		8.5
C	0.1193		89.6
Total,	0.1307		98.1

The hydrocarbons have not, as yet, been identified. The 2 grams of high-boiling residue finally passed over when heated with a free flame, leaving practically no residue, when the thermometer finally rose to 335°. This high-boiling portion is not a hydrocarbon.

The result shows that, while the gaseous products are related to the original body in a very simple manner, the liquid remainder is by no means as simple. A large portion consists of hydrocarbons of high boiling-point, so that the result of the decomposition has been the coupling of the residues. The saponifiable portion, which yields the benzoic acid, is probably phenyl benzoate. Hitherto the amount of substance at our disposal has been too small to follow out this interesting decomposition in such a way as to identify the liquid portion, but we intend to return to this question in the near future, and clear up the mechanism of this change as well as the decomposition of other peroxides by heat, for the reaction may be made one of great synthetic importance. The simplest change,

$$C_6H_5CO.OO.COCH_3 \quad\longrightarrow\quad C_6H_5CO.O|O.COCH_3 \quad\longrightarrow$$
$$C_6H_5CO.OO.COCH_3 \qquad\qquad C_6H_5CO.O|O.COCH_3$$
$$C_6H_5|CO\;O|O\;CO|CH_3$$
$$C_6H_5|CO\;O|O\;CO|CH_3{}'$$
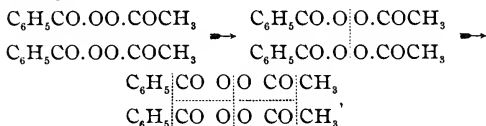
by which diphenyl and ethane would be produced, does not take place, and it is a remarkable fact that the methane, which must unquestionably be produced from one of the methyl groups by reduction of a second methyl group, should result at all, in preference to ethane. The further study of the decomposition-products will probably do much to clear up the constitution of organic acid peroxides.

The above results having fully established the feasibility of determining the quantity of benzoyl acetyl peroxide which can be produced by passing air through a mixture of benzal-

dehyde and acetic anhydride, we first made the following blank test :

Twelve test-tubes were each filled with a mixture of 5 grams of benzaldehyde and 5 grams of acetic anhydride, both dry, and a current of thoroughly dried air was slowly passed through all the tubes at once, placed in series. The first six tubes were opened at intervals of one-half hour, and the contents tested for peroxide. The amount scarcely increased after the first half hour, when 1 cc. of gas only could be collected. One of the tubes was then opened and a small piece of filter-paper, from which the fat had been extracted, placed in it, with the result that the peroxide production increased by 200 per cent in two hours. The tubes which had run for about eighteen hours finally solidified to benzylidene diacetate. This test shows that, unless surfaces other than those of the test-tube and delivery-tube are present, the production of peroxide is very slow, despite the large quantity of air which is run through in six hours. An equilibrium is finally reached in which peroxide is destroyed as fast as it is formed. The paper surface instantly produces a marked increase.

The same series of tubes were now cleaned thoroughly, dried, and each filled again with the same mixture. Pieces of pure metal, in strips, were now dropped in, care being taken to have the surface approximately the same in all, and the strips so placed that the entering air would come in contact with them. The current was admitted during fifteen hours, temperature 12°, when the tubes were taken out, the air stopped, and the peroxide present in each estimated in turn. By this method the tube opened last stood twelve hours, without air being admitted.

Tube.	Contents.	Gas delivered. cc.	Absolute quantity of peroxide. Gram.
1	Aluminum	12.79	0.2055
2	Extracted filter-paper	10.43	0.1691
3	Blank	4.14	0.0670
4	Magnesium	9.76	0.1580
5	Iron	7.83	0.1267
6	Copper	5.76	0.0732
7	Tin	1.56	0.0256
8	Platinum	0.31	0.0050

The accelerating effect of the surfaces is very apparent in

the first portion of the series, but the gradual decrease of peroxide present the longer the tubes were allowed to stand before determining the gas given off, makes it evident that decomposition of the peroxide takes place, and becomes evident as soon as the current of air ceases. As a consequence we repeated the above series, placing the tubes in the current of air successively after a given interval of time, then allowing each tube to be subjected to the action of air for the same length of time, twenty-two hours and forty minutes, removing each in the order in which it was placed in series, and determining the gas at once. Each tube, therefore, stood the same length of time as all of the others.

Tube.	Contents.	Gas delivered. cc.	Absolute quantity of peroxide. Gram.
1	Aluminum	7.2	0.11656
2	Extracted filter-paper	13.6	0.2201
3	Blank	6.4	0.1036
4	Magnesium	63.2	1.0232
5	Iron	40.5	0.6556
6	Copper	1.7	0.0275
7	Tin	13.4	0.2169
8	Platinum	15.2	0.2460

During this reaction the iron (2.728 grams) lost 0.0064 gram, the aluminum 0.0006 gram from 1.485 grams, and the copper 0.064 gram from 2.366 grams. The copper was decidedly attacked, therefore, whereas all other metals were only altered, if at all, to a slight extent. In order to test whether the fact that the metal was attacked would, in the case of copper, reduce the yield, we carried out a series of experiments with copper alone.

Pieces of copper of equal size, previously completely reduced in a current of hydrogen, were placed in the tubes and the following results obtained :

Time of determination after first admitting air. Hours.	Cc. of gas obtained.
2	2.7
4	6.7
6	4.1
8	3.7
10	3.0
12	2.8
14	2.8
24	2.5

It is evident from this that in the case of copper the formation of peroxide rapidly increases to a maximum, the rate of decomposition then exceeds that of formation until a practical equilibrium is reached after twenty-four hours. The metal is attacked in all cases, but the cause of the decomposition is not to be found in the copper acetate produced, because a tube containing copper acetate only gave 11.9 cc. gas after fifteen hours. This peculiar decomposition of copper will be the subject of future investigations.

The above results show, beyond a doubt, that the rate of formation of peroxide is dependent upon the surface action of substances coming in contact with air and the mixture of benzaldehyde and acetic anhydride at the same time, for the blank tubes, in each case, produce no greater quantity of peroxide than would naturally be expected from the surface of glass exposed. Of all substances used, magnesium seemed to have the greatest effect, so that this metal was used in an experiment carried out with the purpose of determining whether absolutely dry air can form benzoyl acetyl peroxide with a mixture of absolutely dry benzaldehyde and acetic anhydride.

The apparatus consisted of a drying train consisting of a worm tube with sulphuric acid, a tube 3 feet long filled with glass wool dusted over with phosphorus pentoxide, and a tube 4 feet long filled with freshly glowed soda-lime, a reaction tube with the entrance tube for air sealed in and surrounded by a spiral of pure magnesium ribbon, and the exit tube sealed to the side and connected to the aspirator by means of a tube 3 feet long, filled with glass 'wool and phosphorus pentoxide. The exit tube of the reaction flask was connected by means of a T, with two distilling flasks which were so adjusted that the first and last portions of the distillate could be run off through side stop-cocks, while any quantity of liquid necessary could be introduced into the reaction flask. All parts of the apparatus were sealed together so as to form a continuous piece of glass. The acetic anhydride used was allowed to stand over sodium for several weeks; the benzaldehyde was distilled several times. The apparatus was heated for several hours at 150°, with a current of air passing through, the acetic anhydride and benzaldehyde were then placed in the distilling flasks and

distilled over into the reaction tube, the first portion of the distillate being rejected in each case, and the tube connecting with the apparatus was then fused off. A slow current of air was then passed through for twelve hours.

Ten cc. of mixture gave 12 cc. of gas, corresponding to 0.1952 gram of peroxide. The presence of moisture is, therefore, not necessary in the formation of benzoyl acetyl peroxide. In this experiment 1.234 grams of magnesium were used, which lost only 0.0041 gram during the time of the reaction, and this loss is probably entirely due to the formation of oxide, during the heating and drying, which was removed during the process of cleaning. The magnesium is, therefore, not acted on during the twelve hours of the experiment, although acetic acid must be produced according to any view which we can take of the formation of benzoyl acetyl peroxide from mixtures of acetic anhydride and benzaldehyde. The same result was obtained in other cases when air was run through the mixture for a sufficient length of time to produce acetic acid enough to more than dissolve all the magnesium present. Nef's view[1] of the formation of benzoyl acetyl peroxide supposes that, in the presence of water, benzaldehyde adds the latter to form dioxytoluene :

$$C_6H_5CHO + HOH = \begin{matrix} C_6H_5 \\ \diagdown \\ H \end{matrix} C \begin{matrix} \diagup OH \\ \diagdown OH \end{matrix},$$
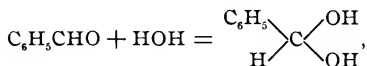
which again separates as follows :

$$\begin{matrix} C_6H_5 \\ \diagdown \\ H \end{matrix} C \begin{matrix} \diagup OH \\ \diagdown OH \end{matrix} = \begin{matrix} C_6H_5 \\ \diagdown \\ HO \end{matrix} C \diagdown + H_2O.$$
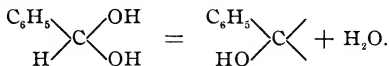
The latter substance then again acts on water to form orthobenzoic acid and hydrogen :

$$\begin{matrix} C_6H_5 \\ \diagdown \\ HO \end{matrix} C \diagdown + 2HOH = \begin{matrix} C_6H_5 \\ \diagdown \\ HO \end{matrix} C \begin{matrix} \diagup OH \\ \diagdown O \ H \end{matrix} + 2H.$$
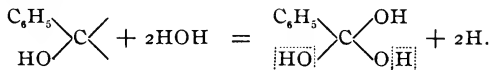
The hydrogen then forms hydrogen peroxide with molecular oxygen, while the benzoic acid forms benzoyl acetyl oxide with acetic anhydride. Finally, hydrogen peroxide is sup-

[1] Anu. Chem. (Liebig), **298**, 280.

posed to oxidize benzoyl acetyl oxide to benzoyl acetyl peroxide.

In view of what has been shown above as regards the ease with which benzaldehyde adds acetic anhydride to form benzylidene diacetate, it seems scarcely credible that, even in the presence of a trace of water, the benzaldehyde should add the latter substance in preference to the former. Nef's view of the mechanism of the reaction must, however, be definitely abandoned after the above demonstration that water is not a necessary factor in the formation of benzoyl acetyl peroxide. The intermediate formation of benzoyl acetyl oxide also does not necessarily accompany the action of air on the mixture of aldehyde and anhydride because, as will be shown below, we have succeeded in so conducting the oxidation as to obtain a crude peroxide which crystallizes completely with only a minimal formation of benzoic acid. Were benzoyl acetyl oxide present in any quantity, it would either manifest itself by being present as an oil mixed with the neutral crystals of peroxide, or, if it were hydrolyzed, its decomposition would show itself by the presence of benzoic acid.

The most reasonable and simple way in which to look upon this oxidation is to assume the existence of an equilibrium between the keto and enol forms of benzaldehyde. The latter would then manifestly add oxygen to form benzoperacid,

$$\underset{HO}{\overset{C_6H_5}{\diagdown}}C\diagup + O_2 = \underset{H-O}{\overset{C_6H_5-C-O}{\diagup\diagdown}}\underset{O}{\overset{|}{\diagdown}} = \underset{O}{\overset{C_6H_5}{\diagdown}}C-O-O-H,$$
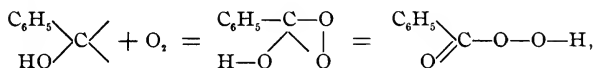
which, in turn, would react with acetic anhydride to form benzoyl acetyl peroxide.[1] This view of the reaction would not affect the question as to the structure of benzoperacid, because formula II., which is the more probable one, can easily result from I. by a rearrangement similar to those so frequently observed in organic chemistry. In any event, the structural formulas of hydroperoxide and the organic peroxides are as yet undetermined, although the weight of evidence

[1] Clover, working in one of the laboratories (Freer's), has shown that benzoperacid may be tested for quantitatively by yielding benzoyl acetyl peroxide upon the addition of acetic anhydride. With solutions of the latter peroxide it yields benzoperoxide.

points toward a symmetrical structure, so that this question must be a subject for future investigation. The above results are in accord with those obtained by Baeyer and Villiger[1] on the oxidation of benzaldehyde. The views of Erlenmeyer, Jr.,[2] Jorissen,[3] and Engler and Wild[4] are all based on the supposition that benzoyl peroxide is the result of the oxidation of a mixture of benzaldehyde and acetic anhydride, and are consequently to be rejected because benzoyl peroxide is only a secondary product of the reaction, for we have convinced ourselves that acetic anhydride cannot convert benzoyl peroxide into benzoyl acetyl peroxide. The supposition of Erlenmeyer, Jr.,[5] that possibly an addition-product of benzaldehyde (benzylidene diacetate) is first formed, which latter substance is then oxidized to a substance which is converted by the mixture into benzoyl peroxide and acetic acid is also not correct, for benzylidene diacetate cannot be oxidized to a peroxide either by air or by hydrogen peroxide. The same view in regard to the mechanism of the reaction was advanced by Bodländer[6] and by Michael,[7] both of whom assumed the existence of benzoperacid,

$$C_6H_5CO.O.O.H,$$
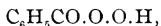
before its discovery by Baeyer.

The above experiments also prove conclusively that the formation of peroxides is remarkably accelerated when certain surfaces are present as catalyzers, and that this influence varies with the nature of the surface. In order to prove that the extent of liquid surface exposed is not of influence, a mixture of equal quantities of benzaldehyde and acetic anhydride was placed in a Fernbach flask so that the bottom was covered to a depth of about 3 mm. The flask was allowed to stand for twenty-four hours, at the end of which time only a very small quantity of peroxide had been formed. The same mixture formed in a large, flat watch-glass, and then drained off,

[1] Ber. d. chem. Ges., **33**, 1582.
[2] *Ibid.*, **27**, 1961.
[3] Ztschr. physik. Chem., **22**, 58.
[4] Ber. d. chem. Ges., **30**, 1677.
[5] *Ibid.*, 1961.
[6] Ahrens Vorträge, **3**, 471.
[7] J. prakt. Chem., **60**, 75.

so that a very thin layer was left, so thin that direct contact of the air with the glass surface was possible, was completely oxidized to a mixture of benzoic acid and benzoyl acetyl peroxide within five minutes.

These results prove conclusively that the oxidation of mixtures of benzaldehyde and acetic anhydride cannot be referred in any great measure to a partial dissociation of the ordinary oxygen of the air, as is supposed by van 't Hoff.[1] As this acceleration of the rate of oxidation is brought about by a variety of surfaces, such as sand, paper, cloth, cotton, and various metals, it seems probable that the oxygen of the air, when occluded by any surface, is rendered chemically more active, and this increased activity is due to a partial dissociation of the occluded oxygen molecules

$$O=O \ = \ O-O.$$
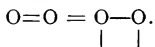
This view is of great importance from a biological standpoint, as, for example, the ease with which hemoglobin is changed to oxyhemoglobin in the lungs can be referred to the large surface of tissue exposed. If the assumption of an equilibrium between the keto and enol forms is correct, then the difference between the activity of various surfaces can be explained by the assumption that the substances introduced into the mixtures of aldehyde and anhydride have different effects on the rate of change from the keto to the enol form, whereas the surface action on the oxygen remains alike in all.

The above experiments clearly indicated to us the best means of procuring any desired quantity of benzoyl acetyl peroxide.

A mixture of equal weights of benzaldehyde and acetic anhydride is prepared, the mixture placed upon strips of filter-paper or muslin, hung in a large glass jar with a cover, and dry air gradually run through. Care must be taken not to place too many strips in the jar at one time, as contact combined with the rapid formation of peroxide will in a very few minutes bring about local heating to such an extent that the paper chars, and may even take fire. After the odor of benzaldehyde has disappeared, the paper or cloth is extracted with

[1] Ztschr. physik. Chem., **16**, 411.

low-boiling petroleum ether, the solution washed with a little soda solution until the washings just become alkaline,[1] then the petroleum ether is partly distilled off from a bath of lukewarm water (the bath must not exceed 80° in temperature, otherwise explosion may result), and the solution is then placed in a freezing-mixture. Crystals of benzoyl acetyl peroxide soon separate, and can be filtered off and recrystallized from the same solvent. On concentrating the petroleum ether further crops of crystals, somewhat less pure, are obtained. The yield often reaches 68 per cent of the theoretical. It varies with the temperature, rate of admission of air, thoroughness of drying, and amount of sunlight. Benzoyl acetyl peroxide thus obtained is identical with that described by Nef. When pure it can be kept apparently indefinitely, provided no moisture comes in contact with it. In the presence of impurities, such as moisture, traces of alcohol, ether, or acids, it gradually decomposes, becoming liquid and then slowly depositing crystals of dibenzoyl peroxide. The liquefaction seems to be due chiefly to a lowering of the melting-point, brought about by the formation of impurities, either diacetyl peroxide or benzoyl hydrogen peroxide, for the melted portion consists for the most part of benzoyl acetyl peroxide. Tubes sealed up, the contents of which had liquefied as above, showed no pressure, so that oxygen is not given off. These changes will be the subject of future investigation. The melting-point of pure benzoyl acetyl peroxide is 40° to 41°.

Pure benzoyl acetyl peroxide is not an oxidizing substance, nor has it any odor, a fact which was also observed by Baeyer.[2] The following experiments will make this clear.

Twenty grams of benzoyl acetyl peroxide were dissolved in 200 cc. of absolute ether, and then 10 grams of aniline were added, and the well-stoppered flask allowed to stand in icewater for twelve hours. At the end of this time 3.5 grams of a solid, which proved to be acetanilide, had crystallized out.

[1] But a very small amount of benzoic acid is produced. This proves that under these conditions but little benzoyl acetyl oxide is formed, for this substance is hydrolyzed by moist air, and the resulting benzoic acid would appear in the alkaline solution.

[2] Ber. d. chem. Ges., **33**, 1574.

The ether was filtered off and evaporated to one-third its bulk, in the cold, and 250 cc. of ligroin were then added. There separated 10.5 grams of a red solid. This was extracted with sodium carbonate solution, which was then acidified, giving a crystalline precipitate of benzoic acid. The remainder was boiled with water until no more dissolved and the water decanted from a dark-red, insoluble oil. The substance crystallizing from the water was acetanilide. The dark-red oil, when recrystallized from ligroin, melted at 34° to 35° and was azoxybenzene.

The ligroin-ether solution was evaporated *in vacuo* in the cold, and the remainder extracted with low-boiling petroleum ether (40°), and the ether evaporated. The remainder had the penetrating odor of benzoyl hydrogen peroxide. It was taken up in ice-cold caustic soda, leaving a residue of benzoyl peroxide, which was filtered. The cold caustic soda solution was then precipitated with barium chloride, yielding a small quantity of a precipitate which decomposed on standing over night at 0°. It was probably benzoperacid. All of the crude acetanilide which separated gave a sharp odor of phenylisonitrile on warming with alkalies pointing to the intermediate formation of phenylhydroxylamine, but not enough of this substance was present to be isolated. In all there were obtained in a pure state 9.3 grams acetanilide, 4.7 grams benzoic acid, 2.5 grams azoxybenzene, 0.5 gram benzoyl peroxide, and traces of benzoperacid. In another experiment in which we used one-half as much peroxide, we were able to isolate 3 grams of aniline benzoate also, with the other products the same, except that no benzoperacid could be detected. The first change in this reaction, which is very gradual, is always the separation of acetanilide, and no oxidation takes place until this change has begun. This fact proves conclusively that the benzoyl acetyl peroxide is not in itself capable of oxidizing aniline, but that it must first be separated into benzoperacid and acetanilide before its oxidizing action can become apparent. The benzoperacid then changes the aniline to azoxybenzene, probably with the intermediate formation of phenylhydroxylamine, while it is itself converted to benzoic acid. If an excess of peroxide is present, then some benzo-

peracid can be isolated. At the end of the reaction, if an excess of aniline is used, then aniline benzoate appears.

Pure benzoyl acetyl peroxide does not produce any marked effect on hydroquinone in benzene for forty-eight hours, if water is excluded ; after this time oxidation gradually sets in with the production of quinhydrone. That a change finally sets in is probably due to the fact that a minute quantity of water, which cannot be excluded in sealing up a flask, gradually causes hydrolysis with the formation of benzoperacid, while the latter oxidizes the hydroquinone to quinhydrone and water, so that the reaction, once begun, would go on with increasing velocity.

Although pure benzoyl acetyl peroxide is not capable of oxidizing action, the aqueous solutions are, for they promptly liberate iodine from potassium iodide. This difference between the normal solid and the solution is due to hydrolysis. This change was followed out quantitatively in the following manner :

Ten flasks, with necks drawn out for sealing, were filled with 2 grams each of benzoyl acetyl peroxide and 100 cc. of water. The containers were then filled and placed in a shaker kept at 26° in a thermostat. The flasks were opened in the order given in the following table, the contents filtered, and the active oxygen in solution determined by means of acid potassium iodide and titration with N/20 sodium thiosulphate. In a certain number of flasks the solid residue was weighed to determine the point at which equilibrium, if any, was reached :

Hours.	Thiosulphate.	Active oxygen in solution.	Benzoyl acetyl peroxide represented.	Solid left.	Active oxygen in solid.	Total active oxygen.
18	44.098	0.0353	0.3967			
24	50.125	0.041	0.4611	1.49		
30	71.335	0.057	0.642			
48	84.04	0.067	0.756	1.31		
72	135.0	0.108	1.22	0.91		
·96	147.34	0.118	1.326			
120	149.41	0.1195	1.345			
144	156.25	0.125	1.407	0.7011[2]	0.0464	0.1714
216	155.6	0.1245	1.326	0.7166[2]	0.0469	0.1715
404	138.9[1]	0.1112	1.259	0.7467[2]	0.0494	0.1606

[1] Slight pressure in tube on opening.

[2] Pure benzoyl peroxide.

Calculated total active oxygen in 2 grams of benzoyl acetyl peroxide, 0.1778.

The solid, after twenty-four hours, melted for the most part at 39° to 40°, only a small portion having a higher melting-point, the amount of benzoyl peroxide gradually increased until, after one hundred and forty-four hours it melted at 106° to 107° sharp, and was pure benzoyl peroxide. Before this time the residual solid was a mixture of benzoyl peroxide and unchanged benzoyl acetyl peroxide, so that, as the relative proportions were unknown, it was impossible to calculate the amount of active oxygen remaining. After all had been converted to benzoyl peroxide, as was the case in the last three experiments, it was possible to calculate the active oxygen remaining in the solid and add it to that found in titrating the solution, and the sum of these two quantities determines whether active oxygen is lost during the hydrolysis. As will be seen from the last column, no such loss took place until four hundred and eight hours were reached, when the tube showed slight pressure on opening. The total quantity of active oxygen present in the benzoyl acetyl peroxide therefore remains after the hydrolysis.

Benzoyl acetyl peroxide, at room temperatures, is slowly attacked by normal caustic soda or caustic potash, giving off oxygen and depositing benzoyl peroxide, which latter is quite stable in the cold, a fact which was also observed by Nef.[1] Baeyer demonstrated that the acid sodium salt of benzoperacid also rapidly gives off oxygen and leaves sodium benzoate and benzoyl peroxide,[2] and to explain this change he assumes that 3 molecules of benzoperacid form one of benzoyl peroxide and one of an oxygenated benzoperacid, which latter then decomposes into oxygen and benzoic acid :

$$C_6H_5CO.O.OH$$
$$C_6H_5CO.O.OH = C_6H_5CO.O.O.COC_6H_5 +$$
$$C_6H_5CO.O.OH \qquad\qquad C_6H_5CO.O.O.O.H + H_2O.$$
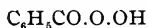
If this same reaction were to take place in aqueous solution, then, as there is no loss of oxygen in the above experiments,

[1] Ann. Chem. (Liebig), **298**, 285.
[2] Ber. d. chem. Ges., **33**, 1570.

we would have to assume that the oxygenated benzoperacid is stable except in the presence of alkalies, and that the primary result is the hydrolysis of benzoyl acetyl peroxide to benzoperacid and acetic acid. It will be shown that this is not correct.

If Baeyer's equation is correct, then the 2 grams of benzoyl acetyl peroxide hydrolyzed above should, when equilibrium is reached, leave 0.89 gram of benzoyl peroxide as an insoluble remainder, and the solution should contain 0.1143 gram of active oxygen. However, as will be seen from the table, the complete change to benzoyl peroxide, when all benzoyl acetyl peroxide has disappeared, results after one hundred and forty-four hours, and then leaves only 0.7 gram, approximately, of benzoyl peroxide, and 0.125 gram active oxygen in solution. This would more nearly represent a change in which one-fourth the active oxygen had separated as benzoyl peroxide.

Another view of this change was, *a priori*, not unreasonable, namely, that benzoyl acetyl peroxide suffers gaseous dissociation into the anions of benzoic and acetic acids,

$$C_6H_5CO.OO.COCH_3 = C_6H_5\overset{-}{C}O.O + CH_3\overset{-}{C}O.O,$$
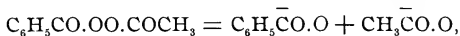
and that the two benzoic acid ions then unite to form the insoluble benzoperoxide, leaving the acetic acid anions as the active constituent. This view is not tenable, however, because:

1. The amount of benzoyl peroxide formed would then contain one-half the active oxygen. Two grams of benzoyl acetyl peroxide in the above experiment should yield, if all the benzoyl was converted into benzoyl peroxide, 1.344 grams of the latter instead of 0.75 gram as found.

2. Benzoyl peroxide is produced from the clear solution, after filtering.

3. Dilute solutions of benzoyl acetyl peroxide in absolute ether or petroleum ether, even after standing thirteen days, deposited unchanged peroxide on evaporation.

4. The molecular weight determination in benzene, even at great dilution, gave numbers so near the theoretical that no

conclusion as to dissociation could be drawn. Found, M 169; calculated, M 180. This difference is no greater than was found to be true for naphthalene in solution in the same benzene and at the same concentration.

The explanation which we have to offer for the changes which occur in solutions of benzoyl acetyl peroxide is briefly as follows:

The hydrolysis of benzoyl acetyl peroxide occurs in two directions, resulting in the formation of benzoperacid and acetic acid on the one hand, and acetoperacid and benzoic acid on the other. These changes can be represented by the equations:

(1) $C_6H_5CO.O.O.COCH_3 + HOH =$
$$C_6H_5CO.O.O.H + CH_3.CO.OH;$$

(2) $C_6H_5CO.O.O.COCH_3 + HOH =$
$$C_6H_5CO.OH + CH_3.CO.O.O.H.$$
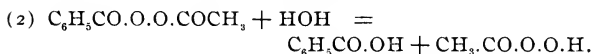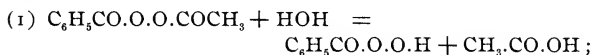
From recent investigations made for us by Mr. Clover it appears that the hydrolysis represented in equation (2) takes place more readily than that represented in equation (1). Moreover, the secondary reaction resulting in the formation of benzoyl peroxide is due to the action of benzoperacid formed in (1) upon the still unchanged benzoyl acetyl peroxide. Thus:

(3) $C_6H_5CO.O.O.COCH_3 + C_6H_5CO.O.O.H =$
$$C_6H_5CO.O.O.COC_6H_5 + CH_3.CO.O.O.H.$$
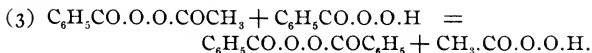
It is to be assumed that of four molecules of benzoyl acetyl peroxide which pass into solution, one remains unchanged, one is hydrolyzed according to equation (1), and two are hydrolyzed according to equation (2), it follows that the resulting benzoyl peroxide as formed in (3) will contain one-fourth the active oxygen present. This, it will be noted, corresponds to the amount actually found by experiment, the details of which are given in the preceding table.

The hydrolyzed solution of benzoyl acetyl peroxide, therefore, yields an insoluble precipitate of benzoyl peroxide and a clear liquid which contains acetic and benzoic acids, some benzoperacid, and chiefly acetoperacid. The presence of ben-

zoic acid is indicated by its crystallization from cooled, concentrated hydrolyzed solutions. Attempts to produce benzoyl peroxide by the action of benzoic acid upon benzoperacid gave negative results.

The amount of benzoperacid in the fully hydrolyzed solution will vary with the condition of hydrolysis. Obviously, if the reaction (3) is retarded it will result in the formation of an excess of benzoperacid over and above what is necessary to combine with the unhydrolyzed peroxide. Under such conditions the solution may contain 10 to 20 per cent of the active oxygen in the form of benzoperacid. On the other hand, conditions which hasten reaction (3) yield solutions containing little or no benzoperacid. It is evident, therefore, that the chemically and bacterially active constituent in the hydrolyzed solution of benzoyl acetyl peroxide is acetoperacid, either alone or associated with small but variable amounts of benzoperacid.

The use of solutions of benzoyl acetyl peroxide as germicides rendered a determination of the solubility in water necessary. The best method of arriving at accurate results was to decompose the substance with N/20 potassium hydroxide, and to titrate the excess of alkali with N/20 hydrochloric acid. If a weighed quantity of benzoyl acetyl peroxide is treated with an excess of N/20 potassium hydroxide, and at once warmed on a water-bath until all benzoyl peroxide has disappeared, the results invariably show the neutralization of more than the calculated quantity of caustic potash by 1 or 2 per cent. If, on the other hand, the peroxide is allowed to stand in the cold with the alkali for twenty-four hours, until the benzoyl acetyl peroxide is completely converted to benzoyl peroxide, and the solution is then warmed on the water-bath, the results are very accurate and correspond exactly to those calculated for the production of 2 molecules of acid.

0.2263 gram substance treated with 70 cc. N/20 potassium hydroxide required 10.9 cc. N/20 hydrochloric acid to neutralize. Calculated, 10.9 cc.

0.2518 gram substance treated with 70 cc. N/20 potassium hydroxide required 14.3 cc. N/20 hydrochloric acid to neutralize. Calculated, 14.1 cc.

Having established the accuracy of the method, we carried out the following experiments:

The peroxide, purified by several recrystallizations, was finely pulverized and then shaken with water at 25°. The amount of peroxide used did not affect the results, but the time of shaking did. It was necessary to shake for two or three minutes until a maximum solubility was reached. The increase in the amount in solution with length of shaking is due to the changes shown in the table given above, and, as indicated, the rise is a slow one. Changes of temperature, of course, materially affect the result.

Three-tenths gram substance was shaken with 110 cc. water, at 25°, filtered quickly through asbestos with suction, and 50 cc. removed and treated with 10 cc. N/20 caustic potash. After warming on the water-bath for several hours the excess of caustic soda was titrated.

	Time. Minutes.	Caustic potash required.	N/20 thiosulphate used to determine active oxygen.
1	5	7.2	7.0
2	10	7.3	7.3
3	15	7.4	7.4
4	20	7.5	7.5
5	30	7.7	7.7
6	40	8.2	8.2

The above table shows that for 1 molecule of peroxide in solution there is 1 atom of active oxygen, for the number of cubic centimeters of N/20 caustic potash and N/20 thiosulphate are the same, and 2 molecules of caustic potash in forming 2 molecules of salt from 1 of peroxide are equivalent to 2 molecules of thiosulphate in reducing iodine. This fact confirms the view that the first change is hydrolysis with the production of peracids,[1] as indicated above in equations 1 and 2.

The solubility, after five minutes, is therefore the equivalent of 7.1 cc. caustic potash ± 1 per cent, which corresponds to 0.639 gram per liter. This would represent 0.0568 gram active oxygen per liter. A 1 per cent hydrogen peroxide solution would contain 4.7 grams active oxygen per liter, or

[1] Electric conductivity measurements of solutions of benzoyl acetyl peroxide showed that rapid hydrolysis takes place. With 20,000 ohms' resistance the bridge readings fell from 850 to 340 in twelve minutes.

eighty times as much. Nevertheless, as will be shown below, these dilute solutions of benzoyl peroxide have a much greater germicidal action than even moderately concentrated ones of hydrogen peroxide. The reason for this is, *a priori*, not apparent, for in the one case we have a substance of the formula $H.O.O.H$ and in the other $C_6H_5CO.O.O.H$. The germicidal action is, therefore, not due exclusively to the absolute quantity of active oxygen in unit space, so that some other cause, of which we cannot at present furnish an explanation, must be at the bottom of this remarkable fact. Hydroperoxide, when pure, is practically odorless, benzoperacid and acetoperacid, both of which have the same intense germicidal action, have most penetrating odors, resembling hypochlorous acid. This latter fact suggests a study of hypochlorous acid from the standpoint of a peroxide, $HCl.O.O.ClH$. All of these facts point to a difference between hydroperoxide and the organic acid peroxides which are germicides, which must be a subject of future investigation.

The decomposition of benzoyl acetyl peroxide with sodium ethylate gives benzoperacid and, apparently, no acetoperacid. Seven and a half grams of pure benzoyl acetyl peroxide were dissolved in 200 cc. absolute ether and cooled to $-12°$. 0.94 gram of sodium dissolved in alcohol and cooled to $-12°$ was then slowly added, care being taken to allow no rise in temperature. The solution instantly forms a precipitate which almost solidifies the entire mass. The precipitate was allowed to stand for ten minutes, during which time it gave off some oxygen. Two hundred grams of ice were then added and shaken until all the solid went into solution. The ether was then separated and the remainder, after adding frozen dilute sulphuric acid, was extracted five times with ethyl chloride. On evaporating the ethyl chloride, a solid remained having the intense odor of benzoyl peroxide. This, when treated with sulphuric acid and alcohol, yielded only benzoic ester, and no acetic ester. The solid is, therefore, a mixture of benzoperacid and benzoic acid. It may be possible, by special methods, to isolate acetoperacid.

ACETYL PEROXIDE.

Acetyl peroxide is best prepared as follows: Commercial

barium dioxide is covered with water, cooled in a freezing-mixture, and then acetic anhydride and dilute hydrochloric acid are added alternately in small quantities, with frequent shaking, until all barium dioxide is used up. Care must be taken not to have the liquid alkaline during the reaction. The mixture is finally acidified with hydrochloric acid, which facilitates the separation of acetyl peroxide, and the crystals of the latter body are filtered off, dried, and recrystallized from ligroin.

Seven and one-tenth grams acetyl peroxide were dissolved in 50 cc. of absolute ether and then 1.38 grams of sodium dissolved in the smallest amount of alcohol slowly added, the whole being well shaken and cooled to —20°. The pasty mass was then poured into 2 volumes of cold petroleum ether and filtered on a Brühl filter. When allowed to stand *in vacuo*, a white salt remains which explodes violently when brought into a flame. The salt dissolves in water, but instantly begins to give off oxygen. On acidifying with frozen dilute sulphuric acid, an oil was produced with a most intense odor of oxide of chlorine, which is characteristic of the peracids. The oil was extracted with ethyl chloride and the latter evaporated. A small quantity of oil, with an indescribably intense odor, remained, but it was so volatile that in a few minutes all was gone. This substance is undoubtedly acetoperacid, but it decomposes so rapidly that its isolation in a pure state will be very difficult. Several attempts to obtain larger quantities gave the same result. The explosive sodium salt, mentioned above, soon loses its character, even when placed in a desiccator.

Unlike benzoyl acetyl peroxide, acetyl peroxide, on standing with water, gradually gives off oxygen. Five grams in 50 cc. of water evolved oxygen during one month, and at the end of that period still contained active oxygen. A solution of acetyl peroxide, 1.2 grams in 50 cc. of water, gave the theoretical amount (0.166 gram) of active oxygen on titration, even after standing but a few minutes, so that hydrolysis was practically complete. After seventeen days, however, this active oxygen had fallen to 0.03 gram.

GERMICIDAL ACTION.[1]

It has been pointed out that certain peroxides are chemically indifferent while others are active oxidizing agents. The chemical behavior in this respect offers a very good indication of the action of these bodies upon bacteria. Those peroxides which are chemically inert are also germicidally inactive, and *vice versa*. Before proceeding into a detailed consideration of this aspect, it may be well to obtain a general view, as it were, of the peroxides heretofore mentioned.

Hydroperoxide, $H.O.O.H$;

Benzoyl peroxide, $C_6H_5CO.O.O.COC_6H_5$;

Acetyl peroxide, $CH_3CO.O.O.COCH_3$;

Benzoyl acetyl peroxide, $C_6H_5CO.O.O.COCH_3$.

It will be seen from the above formulas that the three organic compounds possess a symmetrical structure similar to that of ordinary hydrogen peroxide. The latter substance, as is well known, is a fair germicidal agent, especially when strong solutions are employed. On the other hand, benzoyl peroxide is difficultly soluble, does not undergo hydrolysis, has no oxidizing action, and is wholly without effect upon bacteria. When compared with acetyl peroxide and benzoyl acetyl peroxide, however, a remarkable difference is observed. The last two compounds may also be looked upon as chemically and biologically inert, but, unlike benzoyl peroxide, they readily undergo hydrolysis with the production of intense oxidizing and actively germicidal bodies. The hydrolysis of these bodies has already been discussed, and it is sufficient in this connection to indicate that the active peroxides resulting from the hydrolysis of the inactive forms are :

Benzoperacid, $C_6H_5CO.O.OH$;

and   Acetoperacid, $CH_3CO.O.OH$.

These peracids possess, it will be noted, an asymmetrical structure, and, as stated above, they are extremely active not only chemically but also germicidally. In fact, when solutions of these peroxides are tested upon bacteria and the effect

produced is compared with that caused by a solution of hydrogen peroxide of like oxygen content, that is, of equimolecular strength, it will be found that these organic peroxides are at least several hundred times more active than hydrogen peroxide. Inasmuch as the active oxygen contents in such solutions is the same, it is difficult to explain the difference in effects by mere reference, as has been the case heretofore, to nascent oxygen. Either the active oxygen does not directly participate in the reaction, or else we must assume that it is liberated from the organic peroxides with an enormously higher potential energy than is the case in hydrogen peroxide. It should be noted in passing that while hydrogen peroxide loses its available oxygen readily and even violently, on contact with enzymes, blood and other organic fluids, no such rapid disengagement is observable with the peracids. Indeed, the addition of benzoyl acetyl peroxide to blood, while it causes in time the destruction of hemoglobin, yet it does so without visible evolution of gas.

The simplest explanation of the difference in action between the peracids and hydrogen peroxide appears to us to be based upon the behavior of the acid ions. The acetyl and benzoyl ions, just as the sulphuryl ion in Caro's acid, are to be considered as the active groups which, by their avidity for proteids and other chemical substances, induce the pronounced germicidal and oxidizing effects.

The activity of the hydrolyzed solution of diacetyl peroxide is due to acetoperacid, while that of benzoyl acetyl peroxide is due at times wholly to acetoperacid, more often, however, to this peracid plus variable amounts of benzoperacid as has already been explained.

Benzoyl peroxide may be dismissed in a few words. Since it does not hydrolyze it does not exert any germicidal action whatever. This is most clearly seen by the fact that the extremely weak cholera vibrio is wholly unaffected by benzoyl peroxide.

The hydrolyzed solutions of acetoperoxide and benzoyl acetyl peroxide by contrast exhibit remarkable germicidal effects. Thus, solutions containing 0.01, and even 0.005, per cent active oxygen are capable of destroying within a minute

all known disease-producing bacteria, including the spores of such extremely resistant forms as the potato bacillus.

The methods of testing these solutions need not be considered here, inasmuch as they are given in detail in the paper referred to. It will not be out of place, however, to present a few tabulated experiments which will serve to show at a glance the results obtained. In these tables + indicates that a growth resulted, in other words, that disinfection did not occur. On the other hand, — indicates that no growth occurred and hence the germicidal action is manifested. It should be stated, also, that control experiments were invariably made to test the viability of the cultures used for each experiment.

Table I.

Hydrolyzed Acetyl Peroxide (1–600), 0.0226 per cent active oxygen.

	Minutes.						
	1.	3.	5.	10.	15.	30.	60.
B. pyocyaneus	—	—	—	—	—	—	—
B. coli	—	—	—	—	—	—	—
B. typhosus	—	—	—	—	—	—	—
B. diphtheriæ	—	—	—	—	—	—	—
Vib. choleræ	—	—	—	—	—	—	—
S. pyog. aureus	—	—	—	—	—	—	—
Strept. pyogenes	—	—	—	—	—	—	—
Spores anthrax B.	+	—	—	—	—	—	—
" hay B.	+	—	—	—	—	—	—
" potato B.	+	—	—	—	—	—	—

The acetyl peroxide for this experiment was prepared according to the method previously given. It will be seen from the above table that the relatively weak solution possesses energetic germicidal powers. Even a weaker solution will produce practically the same results, which, in that case, are comparable with those given in Tables II. and III.

A comparison with Table IV. will show that a hydrogen peroxide solution containing twice the amount of active oxygen is, nevertheless, a very feeble germicide. Indeed, to produce like results, it would be necessary to use a hydrogen peroxide solution containing 100 to 200 times as much active oxygen as that contained in the peracid solution. Table IV.

also shows the action of a 5 per cent carbolic acid solution on spores, which stands out in marked contrast to the action of the several peroxides.

Table II.

Hydrolyzed Benzoyl Acetyl Peroxide.

	(1–177), 0.05 per cent active oxygen. Minutes.							(1–2940), 0.003 per cent active oxygen. Minutes.						
	1.	3.	5.	10.	15.	30.	60.	1.	3.	5.	10.	15.	30.	60.
B. pyocyaneus	—	—	—	—	—	—	—	+	—	—	—	—	—	—
B. coli	—	—	—	—	—	—	—	—	—	—	—	—	—	—
B. typhosus	—	—	—	—	—	—	—	+	—	—	—	—	—	—
B. diphtheriæ	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Vib. choleræ	—	—	—	—	—	—	—	—	—	—	—	—	—	—
S. pyog. aureus	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Strept. pyogenes	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Spores anthrax B.	—	—	—	—	—	—	—	+	+	+	+	+	—	—
" hay B.	—	—	—	—	—	—	—	—	—	—	—	—	—	—
" potato B.	—	—	—	—	—	—	—	+	+	+	+	+	+	+

In Table II. are given the results obtained with strong and dilute hydrolyzed solutions of benzoyl acetyl peroxide. While the strong solution kills everything almost instantly, the weaker solution (1–3000) destroys the vegetating germs, as a rule, within one minute, but, as might be expected, the spores require an appreciable time.

Table III.

Benzoperacid (1 : 2500), 0.0046 per cent active oxygen.

	Minutes.						
	1.	3.	5.	10.	15.	30.	60.
B. pyocyaneus	—	—	—	—	—	—	—
B. coli	—	—	—	—	—	—	—
B. typhosus	—	—	—	—	—	—	—
B. diphtheriæ	—	—	—	—	—	—	—
Vib. choleræ	—	—	—	—	—	—	—
S. pyog. aureus	—	—	—	—	—	—	—
Strept. pyogenes	+	—	—	—	—	—	—
Spores anthrax B.	+	+	—	—	—	—	—
" hay B.	—	—	—	—	—	—	—
" potato B.	+	—	—	—	—	—	—

The benzoperacid used for the above experiment was prepared in a pure form by the hydrolysis of benzoyl acetyl peroxide by means of sodium ethylate. The result, it will be

seen, is in accord with those given by the hydrolyzed solutions of acetyl peroxide and benzoyl acetyl peroxide.

Table IV.

	Hydrogen Peroxide, (1–1000). 0.05 per cent active oxygen. Minutes.							Phenol. 5 per cent. Minutes.				
	1.	3.	5.	10.	15.	30.	60.	1.	5.	15.	30.	60.
B. pyocyaneus	+	+	+	+	+	—	—	—	—	—	—	—
B. coli	+	+	+	+	+	+	+					
B. typhosus	+	+	+	+	+	+	+	—	—	—	—	—
B. diphtheriæ	+	+	+	+	+	+	+					
Vib. choleræ	+	—	—	—	—	—	—					
S. pyog. aureus	+	+	+	+	+	+	+					
Strept. pyogenes	+	+	+	+	+	—	—					
Spores anthrax B.	+	+	+	+	+	+	+	+	+	+	+	+
" hay B.	+	+	+	—	—	—	—	+	+	+	+	+
" potato B.	+	+	+	+	+	+	+	+	+	+	+	+

The results recorded in Table IV. serve for comparison with those given in the preceding table. Thus, it will be seen that while the hydrogen peroxide solution contains ten times as much active oxygen as the benzoperacid solution used in Table III., the germicidal effect is entirely different.

These few examples serve to illustrate the interesting fact which we have brought out, namely, that while the symmetrical organic peroxides are inert, the asymmetrical peracids easily rank among the most powerful germicidal agents known. For a more extended account of these bodies it will be necessary to refer the reader to the paper which deals especially with their germicidal behavior.

The results given in this paper are by no means complete, but as one of us expects to be away from his work for a year or more, we thought it best to publish the results obtained up to this time. The work in this interesting and large field will be continued in the future and, as we hope, many of the doubtful points cleared up. The bacteriological work will also be continued with this and other bodies of the same class.

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CXXIX.—ON δ-NITROPYROMUCIC ACID.[1]

By Henry B. Hill and George R. White.

In 1888 Hill and Palmer[2] found that δ-sulphopyromucic acid was decomposed by concentrated nitric acid with the formation of the δ-nitropyromucic acid which had been obtained by Klinkhardt[3] a few years previously by the action of nitric acid upon dehydromucic acid. They also found that a neutral body was formed at the same time, which appeared to be a dinitrofurfuran, but the material at their disposal did not enable them to study it in detail. From the β-brom-δ-sulpho- and the β,γ-dibrom-δ-sulphopyromucic acids they obtained the corresponding bromine derivatives of the δ-nitropyromucic acid, and they further isolated the β,β-dibrom-α,α-dinitrofurfuran. Similar acids were obtained a few years later by Hill and L. L. Jackson,[4] and by Hill and Hendrixson[5] from the chlorsulphopyromucic acids.

It seemed to us that the material needed for an extended study of the δ-nitropyromucic acid could be made most conveniently from δ-sulphopyromucic acid, since the methods which were then known for the preparation of dehydromucic acid involved a great expenditure of time and labor. Most of the nitropyromucic acid which we have used was made in this way, but convenient methods have recently been described[6] for making dehydromucic acid in large quantities, and the method of Klinkhardt is now much more economical. Our study of the nitropyromucic acid was not far advanced when it was interrupted by the removal of one of us from Cambridge, and its progress has since been delayed by circumstances beyond our control. Since further collaboration seems to be out of the question, we have thought it best to

[1] The work described in the following paper formed a part of a thesis presented to the Faculty of Arts and Sciences of Harvard University, in May, 1896, by George Rantoul White, candidate for the degree of Doctor of Philosophy.

[2] This Journal, 10, 380; Proc. Am. Acad., 23, 195.

[3] J. prakt Chem., [2], 25, 51.

[4] This Journal, 12, 126; Proc. Am. Acad., 24, 361.

[5] This Journal, 15, 149; Proc. Am. Acad., 25, 2831.

[6] Hill : Ber. d. chem. Ges., 32, 1221; Phelps and Hale : This Journal, 25, 45; Yoder and Tollens : Ber. d. chem. Ges., 34, 3446.

publish in their present incomplete form the results which we have obtained.

Concentrated nitric acid acts upon δ-sulphopyromucic acid at ordinary temperatures and the reaction is completed on gentle warming. The reaction proceeds simultaneously in two directions, but we have been unable to determine the conditions favorable to the formation of either product. Nitropyromucic acid is formed by the replacement of the sulpho group, and at the same time a nitrofurfuransulphonic acid results from a similar replacement of the carboxyl. The former is sparingly soluble in cold water, while the latter can be isolated through its sparingly soluble potassium salt. Both of these bodies are then converted into dinitrofurfuran by the continued action of fuming nitric acid, although the nitropyromucic acid is but slowly attacked unless sulphuric acid is present in considerable quantity.

$$
\begin{array}{ccc}
 & \begin{array}{c} HC-C-COOH \\ | \quad >O \\ HC=C-NO_2 \end{array} & \\
\begin{array}{c} HC=C-COOH \\ | \quad >O \\ HC=C-SO_2OH \end{array} & & \begin{array}{c} HC=C-NO_2 \\ | \quad >O \\ HC=C-NO_2 \end{array} \\
 & \begin{array}{c} HC=C-NO_2 \\ | \quad >O \\ HC=C-SO_2OH \end{array} &
\end{array}
$$
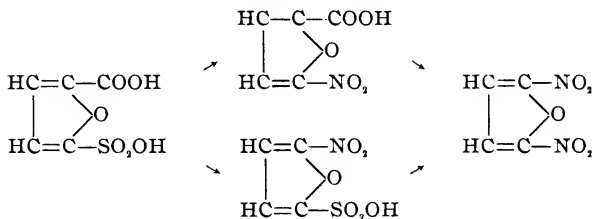
When dehydromucic acid is treated with 10 parts of nitric acid and 1 part of sulphuric acid, as recommended by Klinkhardt, but little dinitrofurfuran is formed.

We have also found that nitropyromucic acid may be made by the action of nitric acid upon a solution of pyromucic acid in fuming sulphuric acid without isolating the sulphonic acid. A saving in time and labor is thus effected, but great care must be taken to avoid any considerable rise in temperature and consequent destructive oxidation.

Nitropyromucic acid forms stable salts, but it is rapidly decomposed by an excess of an alkaline hydrate. With baric hydrate three equivalents were found to be involved in the reaction, baric nitrite being formed, and at the same time a

deep-brown, insoluble barium salt, the nature of which we have not yet determined. Dinitrofurfuran is readily attacked by baric hydrate with the formation of baric nitrite and baric maleate. The reaction is, however, complicated, since the yield of these two salts is but little more than one-half of the theoretical amount, and decidedly less than three equivalents of baric hydrate are used in the reaction. At the same time small amounts of baric carbonate and ammonia are formed. Nitrofurfuransulphonic acid is also decomposed in a similar way in alkaline solution.

We have studied with care two colored bodies which are formed under certain conditions by the action of aniline upon nitropyromucic acid, but we have not yet reached definite conclusions as to their structure. If aniline hydrochloride is added to nitropyromucic acid dissolved in a solution of sodic acetate, reaction soon sets in and a red, insoluble substance is slowly thrown down with the evolution of carbon dioxide. The crude product contains chiefly a yellow body, the formula of which is $C_{16}H_{13}N_3O$, but mixed with a small amount of another substance with the formula $C_{17}H_{13}N_3O_3$. These bodies are evidently formed according to the equations:

$$C_5H_3NO_5 + 2C_6H_7N = C_{16}H_{13}N_3O + 2H_2O + CO_2 \, ;$$
$$C_5H_3NO_5 + 2C_6H_7N = C_{17}H_{13}N_3O_3 + 2H_2O.$$
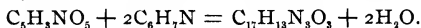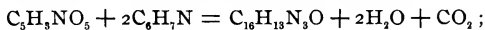
The yellow substance $C_{16}H_{13}N_3O$, which is the main product, is a neutral, indifferent body ; it gives the color reaction of Bülow[1] characteristic for the phenylhydrazones, and yields, when reduced with zinc and acetic acid, ammonia, aniline, and succinanil. These facts seem to warrant the conclusion that the nitro group has been directly involved in the formation of a phenylhydrazone, but further experiments must determine whether the body still contains the furfuran ring intact, or whether its oxygen has already been replaced by the phenylimido group. We have not yet been able to establish experimentally the connection between this body and the crimson substance which contains an additional CO_2. Similar derivatives of paratoluidine were also made.

[1] Ann. Chem. (Liebig), **236**, 195; Cf. V. Meyer : *Ibid.*, **264**, 130; Fischer : Ber. d. chem. Ges., **23**, 384.

Action of Nitric Acid upon δ-Sulphopyromucic Acid.

The δ-sulphopyromucic acid was prepared by exact precipitation of a solution of its barium salt with sulphuric acid. The filtered solution was concentrated on the water-bath, and the acid then thoroughly dried in a desiccator over sulphuric acid. The finely powdered acid was then slowly added with constant stirring to three times its weight of concentrated nitric acid, the specific gravity of which was at least 1.50, carefully cooled with ice. The solution was allowed to stand over night at ordinary temperature, then warmed for a short time, and a part of the nitric acid driven off at a gentle heat. The crystalline mass which was obtained on cooling was treated with a small amount of cold water, drained well with the pump, and washed with a little cold water. This crystalline product is δ-nitropyromucic acid mixed with varying amounts of dinitrofurfuran, while the aqueous solution contains nitrofurfuransulphonic acid. Although nitropyromucic acid and dinitrofurfuran may be separated partially by the use of solvents, we have usually preferred to neutralize the nitropyromucic acid in dilute solution with sodic carbonate, and to remove the dinitrofurfuran completely by extracting the feebly alkaline solution with ether. The nitropyromucic acid is then extracted from the acidified solution with ether and further purified by recrystallization from hot water. The nitrofurfuransulphonic acid can easily be isolated from the acid mother-liquor by neutralizing it with potassic carbonate. The hot solution is a deep red-brown, and on cooling a highly colored potassium salt separates in abundance. The color may be removed by treatment with bone-black, and the potassic sulphate by recrystallization from hot water. A certain amount of the salt may be recovered from the mother-liquors by adding baric acetate in quantity sufficient to convert all the potassic sulphate into acetate and concentrating the filtered solution. The yield of these three products has varied greatly in successive preparations, and we have not been able to determine the precise cause of this variation. The maximum yield of each of the three products, necessarily in different preparations, was about 25 per cent of the sulphopyromucic acid

taken ; ordinarily, however, the amounts obtained were much smaller.

The preparation of the dry δ-sulphopyromucic acid was a simple matter, but we thought that the time involved might be saved by allowing the nitric acid to act directly upon a solution of pyromucic acid in fuming sulphuric acid. At first we found great difficulty in maintaining a sufficiently low temperature, even in experiments conducted on a small scale, but by using a thin, seamless iron dish, set in a freezing-mixture, the reaction could easily be controlled. The iron dish was hardly attacked by the concentrated acids used. One part of pyromucic acid was dissolved in 3 parts of fuming sulphuric acid, the temperature not being allowed to rise above 20°. On the following day, 3 parts of fuming nitric acid of sp. gr. 1.51 were slowly added with constant stirring, the temperature being kept below 40° by means of a freezing-mixture. The product was kept in the freezing-mixture for at least an hour, and was then allowed to stand at ordinary temperature over night. The dinitrofurfuran and nitropyromucic acid were then extracted by ether from the diluted solution, and separated by means of a dilute solution of sodic carbonate, as before. By this method 100 grams pyromucic acid gave 17 grams of nitropyromucic acid and from 6 to 12 grams of dinitrofurfuran, but no nitrofurfuransulphonic acid could be isolated.

Nitrofurfuransulphonic Acid.

As yet we have succeeded in making the nitrofurfuransulphonic acid only by the action of nitric acid on the δ-sulphopyromucic acid, and we have not been able to prepare, from the sparingly soluble potassium salt by means of which we isolated it, any other salts by double decomposition.

Potassic Nitrofurfuransulphonate, $KC_4H_2NSO_6$.—This salt is very sparingly soluble in cold water, readily soluble in hot water, and as the solution cools it is deposited in brilliant, long, flat, rectangular prisms, which are anhydrous.

I. 0.6904 gram air-dried salt gave 0.2585 gram K_2SO_4.

II. 0.6182 gram air-dried salt gave 0.2320 gram K_2SO_4.

III. 0.4730 gram air-dried salt gave 26.2 cc. N over KOH at 27° and under a pressure of 764 mm.

	Calculated for $KC_4H_2NSO_6$.	I.	Found. II.	III.
K	16.92	16.82	16.85	....
N	6.07	....	....	6.20

When treated with twice its weight of concentrated nitric acid, the potassium salt yields dinitrofurfuran in abundance. On heating with distillable hydrobromic acid in a sealed tube, at 100°, it was completely decomposed. The diluted solution, when extracted with ether, yielded a crystalline acid which melted at 160° to 161°, after recrystallization from a small quantity of water, and contained the percentage of bromine required by a bromsuccinic acid.

0.2655 gram substance gave 0.2531 gram AgBr.

	Calculated for $C_4H_5BrO_4$.	Found.
Br	40.58	40.58

Qualitative tests showed that sulphuric acid had been formed, and at the same time the solution reduced cupric oxide vigorously in the cold. The body therefore appeared to have been decomposed according to the equation :

$$KC_4H_2NSO_6 + 3H_2O + HBr = C_4H_5BrO_4 + KHSO_4 + NH_3O.$$
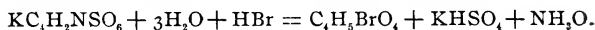
α,α-Dinitrofurfuran.

All the material which we have used was made from pyromucic acid by the methods just described. Dinitrofurfuran is formed, however, in small quantity by the action of nitric acid upon dehydromucic acid, and the amount is apparently increased if sulphuric acid is also added. It may be made from nitropyromucic acid without difficulty by warming it to 60° with concentrated nitric acid to which an equal volume of sulphuric acid is added. The crude product which we obtained by extracting the alkaline solution of nitropyromucic acid with ether was recrystallized from hot alcohol.

I. 0.3250 gram substance gave 0.3603 gram CO_2 and 0.0520 gram H_2O.

II. 0.2793 gram substance gave 41.2 cc. N over KOH at 12°.5 and under a pressure of 780 mm.

	Calculated for $C_4H_2N_2O_5$.	Found. I.	II.
C	30.38	30.24	....
H	1.28	1.79	....
N	17.76	....	17.95

α,α-Dinitrofurfuran is quite readily soluble in ether. It is sparingly soluble in cold alcohol, but dissolves freely on heating. It is readily soluble in benzol or in hot chloroform, but is almost insoluble in carbonic disulphide or ligroin. It dissolves sparingly even in boiling water, volatilizes slowly with steam, and crystallizes from hot aqueous solution in clustered needles. From alcohol it crystallizes in slender prisms which are not infrequently grouped together in feather forms. It is usually pale-yellow, but may be obtained nearly colorless by precipitating its solution in benzol with ligroin. It melts at 101°, and sublimes readily at a lower temperature.

Hill and Palmer noted that a filter-paper moistened with an alcoholic solution of dinitrofurfuran exposed to the vapors of ammonic sulphide was colored yellow at first, then salmon-red. The preliminary experiments which we tried with various reducing agents were so far from encouraging in their results that we have as yet made no more extended study of these products. We have, however, studied more in detail the decomposition which takes place in alkaline solution. Even in the cold, a yellow color is developed and a nitrite is formed ; on heating, the reaction is completed in a short time.

A weighed amount of dinitrofurfuran was dissolved in about 200 times its weight of hot water and an excess of a titrated solution of baric hydrate was then added. A deep-red color was developed which immediately passed into a yellow, and this yellow color slowly faded on boiling. The clear solution gradually grew turbid and a small amount of ammonia was formed. The excess of baric hydrate was then precipitated by carbonic dioxide from the filtered solution, and the baric carbonate thus formed was dried and weighed. Two experiments, in each of which 0.790 gram of dinitrofurfuran was taken, showed that 1.34 and 1.30 molecules of baric hydrate had entered into reaction ; the insoluble salt which had been thrown down in the boiling solution proved to be mainly baric carbonate, but the amount was insignificant, 0.25 and 0.27

molecule in the two cases. On concentrating the aqueous solution, a barium salt separated in flat, obliquely-truncated needles, which appeared to be identical in form and habit with baric maleate ; in the mother-liquor was baric nitrite in abundance. The weights of the baric maleate obtained corresponded to 0.53 and 0.55 molecule respectively. The amount of nitrite formed was determined with separate portions of dinitrofurfuran, and as the mean of two determinations it was found that 62.5 per cent of the nitrogen had been converted into baric nitrite. The baric maleate was decomposed by dilute sulphuric acid, taking care to leave a trace of barium in solution, and the solid obtained by evaporation was then extracted with ether. The acid thus obtained was readily soluble in ether and very soluble in cold water. It melted at 131° to 132°, sublimed readily between watch-glasses, and the last portions of the sublimate melted at 52° to 53°. On evaporation with hydrochloric acid, a sparingly soluble acid was obtained which had all the characters of fumaric acid. In addition, the barium salt was shown to have the composition of baric maleate.

0.5946 gram air-dried salt lost, at 160°, 0.0405 gram H_2O.

	Calculated for $BaC_4H_2O_4 \cdot H_2O$.	Found.
H_2O	6.69	6.81

0.5421 gram salt, dried at 160°, gave 0.5024 gram $BaSO_4$.

	Calculated for $BaC_4H_2O_4$.	Found.
Ba	54.66	54.54

δ-*Nitropyromucic Acid.*

The nitropyromucic acid used was recrystallized from hot water, and agreed in properties with the description of Klinkhardt. In the preparation of salts of the acid we noticed that an excess of an alkaline hydrate immediately brought about a change of color, and that decomposition soon set in at ordinary temperatures. The change of color to a reddish-yellow is sufficiently well marked to serve as an indicator in the titration of the acid. In two successive trials 0.314 gram of the acid required 6.90 and 6.90 cc. of a baric hydrate solution, 1

cc. of which was equivalent to 2.88 cc. N/10 hydrochloric acid ; the calculated amount is 6.94. With an excess of baric hydrate a dark-brown, flocculent precipitate is slowly formed at ordinary temperatures, and the same decomposition takes place at once on boiling ; in either case exactly 1.5 molecules of baric hydrate are involved in the reaction. Baric nitrite is formed in abundance, but we have not succeeded in determining the nature of the insoluble product.

If ethereal solutions of nitropyromucic acid and aniline are mixed, aniline nitropyromucate at once separates in colorless, clustered leaflets. The salt is very sparingly soluble in ether or in cold alcohol, but it dissolves freely in boiling alcohol. On exposure to the air it rapidly turns dark in color. The salt dried in a desiccator gave the following results :

I. 0.2197 gram substance gave 0.4258 gram CO_2 and 0.0831 gram water.

II. 0.4427 gram substance gave 45.8 cc. N over KOH at 25° and under a pressure of 754 mm.

	Calculated for $C_{11}H_{10}N_2O_5$.	I.	II.
		Found.	
C	52.76	52.86	....
H	4.03	4.23	....
N	11.23	....	11.53

This aniline salt is sparingly soluble in cold water and may be recrystallized from hot water. An aqueous solution at ordinary temperature is slowly decomposed with the precipitation of brownish flocks. If aniline is added to the aqueous solution, or better, aniline acetate, the reaction is accelerated, and a voluminous, brilliant-red precipitate is formed after the lapse of a few hours. This body may be prepared more conveniently by adding rather more than 2 molecules of aniline hydrochloride to nitropyromucic acid dissolved in a solution of sodic acetate. The solution should not contain more than 1.5 per cent of the nitropyromucic acid in order that no aniline salt may separate. The solution soon grows turbid and gradually deposits the red body ; at the same time carbonic dioxide is slowly evolved. After standing for forty-eight hours at ordinary temperature the reaction is in great part completed, but the filtered solution again grows turbid and

continues for several days to deposit small amounts of the colored product. The reaction may be accelerated by heat, but the color of the product is then not so brilliant. The weight of the precipitate when dried was usually about 25 per cent more than that of the nitropyromucic acid taken. On closer examination the substance proved to be a mixture of two bodies which could easily be separated by means of chloroform. When thoroughly extracted with chloroform an orange-yellow body was left, which amounted to about 80 per cent of the mixture taken, while the dark-red chloroform solution contained a crimson substance.

The yellow body proved to be very sparingly soluble or insoluble in all ordinary solvents, except glacial acetic acid, in which it was not freely soluble even on boiling. As the solution cooled the body separated in nearly rectangular, four-pointed stars, which were deep-red in color but gave a yellow powder. The material thus purified gave the following results; in analyses IV. and VI. the substance was washed with alcohol and water :

I. 0.2201 gram substance gave 0.5855 gram CO_2 and 0.1004 gram H_2O.

II. 0.2152 gram substance gave 0.5725 gram CO_2 and 0.0974 gram H_2O.

III. 0.2215 gram substance gave 0.5892 gram CO_2 and 0.1019 gram H_2O.

IV. 0.2149 gram substance gave 0.5737 gram CO_2 and 0.0962 gram H_2O.

V. 0.4362 gram substance gave 58.9 cc. N over KOH at 15° and under a pressure of 769 mm.

VI. 0.4846 gram substance gave 65.8 cc. N over KOH at 17° and under a pressure of 773 mm.

	Calculated for $C_{16}H_{13}N_3O$.	I.	II.	III.	IV.	V.	VI.
C	72.95	72.57	72.57	72.54	72.83	....	....
H	4.98	5.10	5.06	5.14	5.01	....	....
N	16.01	....	....	....	....	16.03	16.08

When quickly heated the substance melted at 232°, but this melting-point was lowered several degrees by slow heating. The body was indifferent to aqueous acids or alkalies, but it

dissolved promptly in alcoholic soda or potassic hydrate with the formation of an intense carmine-red color ; on dilution with water the original substance was apparently precipitated. It dissolves in concentrated sulphuric acid to form an orange-yellow solution. The addition of ferric chloride or potassic dichromate develops a deep greenish-blue color. The green tinge is apparently due to the yellow color of the sulphuric acid solution, or to an excess of the oxidizing agent. With ammonic sulphide in alcoholic solution a reduction-product is apparently formed which we have not further examined. Complete reduction is easily effected by the addition of zinc dust to the hot solution in somewhat diluted glacial acetic acid. After removing the zinc the solution gives, on concentration, long colorless needles which are sparingly soluble in cold water. The melting-point, 151° to 152°, and the behavior of the substance showed that it was succinanil, and its identity was established by analysis.

I. 0.2103 gram substance gave 0.5278 gram CO_2 and 0.0990 gram H_2O.

II. 0.3389 gram substance gave 24.1 cc. N over KOH at 20° and under a pressure of 761 mm.

	Calculated for $C_{10}H_9NO_2$.	Found. I.	Found. II.
C	68.53	68.47	....
H	5.18	5.27	....
N	8.02	....	8.18

In the mother-liquor from the succinanil the presence of aniline and ammonia could easily be shown by qualitative tests.

The crimson body was obtained by distilling off most of the chloroform, adding alcohol to the residue, and washing the crystals which were thus separated with cold alcohol. For analysis it was recrystallized from glacial acetic acid, washed with water, and dried over sulphuric acid.

I. 0.1907 gram substance gave 0.4646 gram CO_2 and 0.0740 gram H_2O.

II. 0.3217 gram substance gave 37.4 cc. N over KOH at 16° and under a pressure of 773 mm.

	Calculated for $C_{17}H_{13}N_3O_3$.	Found. I.	II.
C	66.40	66.45	....
H	4.26	4.34	....
N	13.71	....	13.82

This body is sparingly soluble in alcohol or ether, but is readily soluble in chloroform, benzol, or hot glacial acetic acid. From the latter solvent it crystallizes in flattened crimson needles, which melt at 218° when slowly heated, but decomposition apparently sets in at a lower temperature. We have not yet succeeded in preparing serviceable derivatives of this body.

We have also made the corresponding derivatives of para-toluidine. The properties of these bodies are almost identical with those of the aniline derivatives, and they were made and purified by the same methods. The yellow toluidine compound crystallized from glacial acetic acid in clustered prisms which melted at 250° when quickly heated.

I. 0.2226 gram substance gave 0.6053 gram CO_2 and 0.1188 gram H_2O.

II. 0.5060 gram substance gave 65.3 cc. N over KOH at 21° and under a pressure of 750 mm.

	Calculated for $C_{18}H_{17}N_3O$.	Found. I.	II.
C	74.16	74.16	....
H	5.88	5.97	....
N	14.46	....	14.56

On reduction with concentrated acetic acid and zinc dust it gave ammonia, paratoluidine, and a body which melted at 153° to 154°, and had the percentage composition of a tolyl-succinimid.

I. 0.1844 gram substance gave 0.4712 gram CO_2 and 0.0984 gram H_2O.

II. 0.1773 gram substance gave 12.0 cc. N over KOH at 17° and under a pressure of 769 mm.

	Calculated for $C_{11}H_{11}NO_2$.	Found. I.	II.
C	69.79	69.71	....
H	5.86	5.97	....
N	7.44	....	7.97

The crimson compound crystallized from glacial acetic acid in finely felted needles, which were decomposed on heating. When washed with water and dried over sulphuric acid it gave the following results :

I. 0.1651 gram substance gave 0.4124 gram CO_2 and 0.0810 gram H_2O.

II. 0.2233 gram substance gave 24.6 cc. N over KOH at 18° and under a pressure of 760 mm.

	Calculated for $C_{19}H_{17}N_3O_3$.	I.	II.
		Found.	
C	68.01	68.13	....
H	5.11	5.49	....
N	12.57	....	12.77

THE QUANTITATIVE SEPARATION OF HYDRO-CHLORIC AND HYDROCYANIC ACIDS.

By Theodore William Richards and Sidney Kent Singer.

In the course of some recent work which involved the use of very pure potassic cyanide, the lack of a convenient method for determining the amount of chloride present in this salt became manifest. Accordingly, Miss Grace E. Dennett and Miss Selma Hunt, advanced students of chemistry at Radcliffe College, tested a new method, at the request of one of us. Unfortunately, lack of time prevented them from performing all the details necessary for the final judging of the method, but their results were so promising that the matter seemed worthy of further pursuit. This end we have accomplished, and the present paper contains a detailed description of the method.

In seeking to effect any separation, one naturally utilizes an operation which brings into play some property possessed by the two substances to be separated in as different a measure as possible. Now the most striking difference between hydrocyanic acid and hydrochloric acid is the difference in the degree of their ionization. According to Walker and Cormack[1] the "dissociation constant" of a tenth-normal solution of hydrochloric acid is about nine thousand times as great as that of equally concentrated hydrocyanic acid. Both undissociated

[1] J. Chem. Soc., London, **77**, 5 (1900).

acids are very volatile, hydrochloric acid being the more so, but ions have little or no tendency to leave an aqueous solution with steam. Hence it seemed possible that by evaporating a dilute solution of the mixed acids, with continual addition of water, all the hydrocyanic acid might be expelled without the loss of an important amount of hydrochloric acid.

Since some experiments of Richards and Mallinckrodt, as yet unpublished, showed that a tenth-normal solution of hydrochloric acid emits only a negligible amount of hydrochloric acid with its vapor, the solutions were kept at this dilution by the frequent addition of water. The evaporation was effected in vessels of various shapes, all of which gave fairly satisfactory results. The chief disadvantage of an open dish on the steam-bath was the danger of absorbing hydrochloric acid from the air of the crowded laboratory during the protracted evaporation, and the chief disadvantage of a common flask, or of a large beaker with a funnel over it, was the danger of loss of liquid in the minute drops caused by rapid ebullition. We finally decided upon the use of a common untubulated retort of 500 cc. capacity, with its neck directed upwards at an angle of 45°. In this vessel all the analyses given below, except Nos. 5, 6, and 15, were boiled. A large beaker with an inverted funnel over it was used in the three cases named as exceptions. In every case the precipitation was effected in a large beaker.

Experiments with perfectly pure hydrocyanic acid showed that two hours' boiling was enough to expel every perceptible trace of the acid. The cooled solution gave no cloudiness with argentic nitrate.

In the next place a series of experiments was executed with "C. P." potassic cyanide of commerce as the starting-point. A large volume of solution was made up, and for each analysis a quantity containing 1.25 grams of the salt was taken. This material was diluted to the bulk of about 400 cc., and to it were added 5 cc. of sulphuric acid. The mixture was submitted to active ebullition, with the addition of water in such measure as to prevent the volume from ever falling below 300 cc. At the end of a prearranged time the ebullition was stopped and the remaining chloride was precipitated with argen-

tic nitrate. Some time was usually required for the very scanty precipitate to assume an aggregation suitable for filtration.

The table given below records the time of boiling and the weight of argentic chloride found.

No. of experiment.	Time of boiling. Hours.	Weight AgCl found from residue. Gram.
I	2	0.0049
2	3	0.0047
3	3	0.0048
4	4	0.0054
5	$7\frac{1}{2}$	0.0050
6	8	0.0047
7	$11\frac{1}{2}$	0.0050
8	$11\frac{1}{2}$	0.0052

Average, 0.0050

The constancy of figures in the last column is as great as could be expected; it shows that all the acid which could be expelled was driven out at the end of two hours. Thus no essential amount of hydrochloric acid was lost after that time, and since the experiments with pure hydrocyanic acid showed that this acid could all be driven off, the precipitate must have consisted wholly of argentic chloride. Hence the average, 0.0050 gram, is a constant which may be used with future experiments involving the solution.

Two points remained to be proved. Could any of the hydrochloric acid have been carried off during the first two hours, and can the hydrocyanic acid be expelled as readily when much hydrochloric acid is present? Both of these questions may be easily answered by a series of experiments in which a known amount of potassic chloride is added to the standard solution of cyanide. In this series, recorded below, the method of experimentation was precisely similar to that employed in the earlier series. The mixed solution was diluted, treated with an excess of sulphuric acid, and boiled. From each weight of argentic chloride obtained from this solution was subtracted 0.0050 gram, the correction found above :

No. of experiment.	Weight KCl added. Gram.	Weight AgCl calculated. Gram.	Weight AgCl found (corr.). Gram.	Error. Milligrams.	Time of boiling. Hours.
9	0.0862	0.1657	0.1984	+32.7	2.0
10	0.2883	0.5541	0.5628	+ 8.7	4.0
11	0.0811	0.1558	0.1604	+ 4.6	4.0
12	0.0946	0.1819	0.1832	+ 1.3	6.0
13	0.0699	0.1343	0.1359	+ 1.6	8.0
14	0.0696	0.1338	0.1337	− 0.1	9.0
15	0.0653	0.1255	0.1262	+ 0.7	9.5
16	0.1738	0.3341	0.3342	+ 0.1	9.5
17	0.1282	0.2464	0.2472	+ 0.8	10.0

These results bring out several interesting points. In the first place, two hours' boiling, which amply sufficed when little or no potassic chloride was added, is now entirely inadequate to expel all the hydrocyanic acid. Thus, something in the solution must tend to hold back this acid. But the only important addition to the solution is the chlorine ion, hence the chlorine ion must tend to form a complex with hydrocyanic acid. The tendency of this ion to form complexes with various other undissociated groups has been noticed before, especially by Richards and Archibald,[1] so that this behavior is not startling, but it is nevertheless a matter of interest which will receive further attention in this laboratory.

Of more direct bearing upon the immediate object of the present research is the fact that after eight or nine hours' prolonged boiling this complex seems to be entirely broken up by progressive dissociation due to the steady volatilization of one of its components, and that this volatilization is effected without loss of hydrochloric acid. Thus it is shown that the method really affords a convenient and adequate means of separating quantitatively the two acids in question. Probably hydrobromic acid could be separated as easily as hydrochloric.

While the hydrocyanic acid might be collected and determined in the distillate, it would probably be easier to determine the amount by difference, precipitating both in one portion as argentic salts, and then precipitating argentic chloride alone in another portion, which had been evaporated in the manner described in this paper. The silver salts are so easily

[1] Proc. Am. Acad., **37**, 347 (1902).

weighed that this indirect method would not lead to serious error.

The outcome of this paper may be summed up as follows : A simple method is described for the quantitative analysis of mixtures of chlorides and cyanides, and evidence is given which indicates a tendency on the part of hydrocyanic acid to add to the chlorine ion.

CAMBRIDGE, MASS., Jan. 27, 1902.

ON THE NATURE OF MERCURIC IODIDE IN SOLUTION.

BY J. H. KASTLE AND JEWETT V. REED.

About two years ago it was shown by Kastle and Clark[1] that solutions of mercuric iodide in organic solvents have a yellow color and that from such solutions the yellow form of the iodide and not the red separates on crystallization. The effect of heating the red mercuric iodide with amyl alcohol, keeping the iodide in excess, was also tried. It was observed that a yellow solution of mercuric iodide was always obtained and that invariably a thin film of the yellow variety, or a little mass of yellow crystals, was found on top of the unchanged red iodide. The view was advanced, therefore, that when equilibrium is reached in such solutions there are as many molecules passing out of the solution as are passing in, and that both are molecules of the yellow variety of this compound. That the red iodide is not entirely changed to yellow by first passing into solution and then crystallizing out is probably due to the fact that by contact with a certain amount of the red variety remaining in the tube, the yellow is rapidly changed to red as it separates from the solution. We should, therefore, have the solvent constantly changing the red iodide to the yellow, then dissolving it and again precipitating it in the yellow form. This last, however, would tend to pass back to the red modification as soon as removed from solution. It will be observed, therefore, that the effect of solvents on the red iodide of mercury is essentially the same as that produced by heat; and that in the act of dissolving, the transition temperature of the iodide is greatly lowered.

[1] This JOURNAL, **22**, 473, 484.

14–27

In this connection it occurred to us to determine whether the yellow form of mercuric iodide could exist in equilibrium with its solution at temperatures below its transition-point, *viz.*, 128° C. With this in view, tubes were prepared containing amyl alcohol and red mercuric iodide, the latter in excess of that required to form a saturated solution at the given temperature. These tubes were then heated in the air-oven at 150° C. until a saturated solution of the iodide in amyl alcohol was obtained and until the excess of the iodide had been transformed to the yellow modification. The tubes were then placed in the vapor of boiling glacial acetic acid, 118° C. For some time after putting the tubes into the vapor of the acetic acid the yellow crystals of the iodide showed no alteration. In about ten minutes, however, red spots began to appear among the yellow crystals, indicating that no equilibrium was possible between the yellow variety of mercuric iodide and its saturated solution in amyl alcohol even at 10° below the transition temperature of the compound. These experiments were repeated several times with like result in every case.

Are Solutions of Mercuric Iodide Saturated with the Yellow or Red Modification of the Compound?

As was pointed out in our previous communication, the color of solutions of mercuric iodide is such as to indicate that they are saturated with respect to the yellow variety of this compound only. With the view of throwing still further light on this question, which, from a theoretical standpoint, is one of great importance, the attempt was made to prepare supersaturated solutions of the iodide in certain of these solvents, with the view of testing the conduct of such solutions towards crystals of the red and yellow variety of the compound. Considerable difficulty in the selection of a solvent was encountered at the outset in consequence of the great tendency on the part of the iodide to crystallize. Among the first solvents to be tried was amyl alcohol. It was found, however, that as soon as the supersaturated solutions of the iodide in this solvent were placed in tubes in order to make the necessary observations, a rim of yellow crystals separated on the top of the solution, thereby putting a stop to the experiment. It was found

that this difficulty could be overcome by employing naphthalene. After a number of preliminary observations, it was found that a supersaturated solution of mercuric iodide in naphthalene could be prepared by dissolving 1 part of the iodide in 20 parts of naphthalene. During the filtering of such solutions a small amount of naphthalene was unavoidably lost by evaporation. It was found that this could be compensated for by making the ratio of the mercuric iodide to naphthalene 1 : 20.1 or 1 : 20.25 instead of 1 : 20. As a general thing it was found expedient to make up a sufficient quantity of such a supersaturated solution for a whole series of experiments. This was done by melting 80 grams of naphthalene with the required amount of mercuric iodide in a tightly stoppered bottle. The solution thus obtained was usually slightly turbid and, hence, had to be filtered. This was done by filtering it through a folded filter-paper into another glass bottle, the filter-paper, funnel, and bottle having been previously heated in the air-oven to 140° C. In this manner a perfectly clear, yellow solution of mercuric iodide in naphthalene was obtained. With such solutions, experiments were conducted in the following manner :

A number of test-tubes, 6 x ¾ inches, were graduated in 10 cc. A pair of these tubes were then clamped together as close as possible by means of iron clamps which, in turn, were fastened securely to the wall of the laboratory. A glycerin-bath was then placed under the tubes, on the ring of an iron stand, and so arranged that it could be raised or lowered without disturbing the tubes. The bath, which consisted of a large beaker partly filled with glycerin, was then heated to 140° C., and the tubes so immersed therein as to have the 10 cc. mark on the tubes some little distance beneath the surface of the glycerin. By means of a long-necked funnel 10 cc. of the solution of mercuric iodide in naphthalene, which had been kept at 140° C. in the air oven, were poured into each of the tubes in the glycerin-bath. Thermometers, which had previously been heated to 140° C. in the air-oven, were then placed in the tubes and so arranged that their bulbs were entirely immersed in the solution without touching either the bottom or sides of the tubes. During this time the temperature of the

glycerin-bath was kept at 140° C. When everything had been thus arranged the glycerin-bath was quickly lowered and a bath of boiling water put in its place. This bath consisted of a large beaker about two-thirds full of boiling water and so arranged as to keep the level of the water always above that of the solution in the tubes. In about three minutes from the time the tubes were immersed in the boiling water they had reached a temperature of 100° C., and no mercuric iodide had as yet crystallized out of the solution. A few crystals of the red mercuric iodide, which had also been heated to 100° C., were now carefully dropped into the solution in one of the tubes, care being taken not to jar or shake the tube in any way. No crystals of either variety of the iodide separated on the addition of the red crystals. A few crystals of the yellow iodide, which had been heated to 100° C., were then dropped into the second tube, when a large crop of yellow crystals separated from the solution at once, whereas in the tube to which the red crystals were first added no crystals of any kind had separated up to this time. A few yellow crystals, warmed to 100° C., were then put into this tube, when a large crop of yellow crystals separated immediately. During all this time the tubes containing the solution of mercuric iodide were so immersed in the boiling water as to keep the level of the water always above that of the solution in the tubes. These experiments were repeated several times with exactly the same results in every case. Hence we must conclude that the solution of mercuric iodide in naphthalene is supersaturated with respect to the yellow iodide of mercury and not with respect to the red. That such is the case is borne out by the color of the solution. It was also observed that finely and coarsely powdered glass and powdered calc spar, heated to 100° C., caused the separation of yellow crystals from these supersaturated solutions of mercuric iodide in naphthalene, and a cold particle of almost any kind, or one heated below 100° C., was found to do the same. In view of the great tendency on the part of the mercuric iodide to crystallize, it occurred to us that the separation of crystals of this compound from its supersaturated solutions by the powdered glass and calc spar might in reality have been brought about by a low-

ering of the temperature of the solution by the solid particles
rather than by the action of a truly isomorphous substance on
the solution. Up to this time the substances to be added to
the supersaturated solutions of the iodide had been heated in
small test-tubes on the water-bath. In the last series of ex-
periments on this phase of work the substances intended to
be put into the supersaturated solutions of the iodide were
heated in a small test-tube, surrounded by a steam jacket and
so arranged as to bring the mouth of the small test-tube di-
rectly over the mouth of the larger tube containing the solu-
tion of mercuric iodide. In this way any cooling of the crys-
tals was prevented. The following substances were tried
under these improved conditions :

The yellow and red iodide of mercury, Iceland spar, sodium
nitrate, hematite, siderite, celestite, fluor-spar, carborundum,
and finely powdered glass, coarsely powdered glass, gypsum,
and dolomite. The red and yellow iodide of mercury were
added in the form of small crystals, the other substances in the
form of coarse powder. Of these substances the following
were found to throw out crystals of the yellow iodide of mer-
cury from the supersaturated solutions of mercuric iodide in
naphthalene : The yellow iodide of mercury, finely powdered
glass, Iceland spar, sodium nitrate, siderite, hematite, celes-
tite, fluorspar, and carborundum. On the other hand, the red
iodide of mercury, coarsely powdered glass, gypsum, and
dolomite caused no separation of crystals of any kind from the
supersaturated 'solutions of the iodide. It is interesting to
note in passing that of those substances that precipitate yel-
low mercuric iodide from its supersaturated solution a num-
ber of them are rhombic in crystal form like the yellow iodide
of mercury itself. The fact, however, that the yellow iodide
is also thrown out of its solutions by substances of different
crystal habit and even by sharp-pointed fragments, such as
glass, would seem to indicate that the precipitation of the yel-
low iodide from its supersaturated solutions is not necessarily
brought about by the action of isomorphous crystals but also
by the disturbance of an unstable condition of equilibrium in
the supersaturated solutions of the iodide. That such is the
case would also seem to be indicated by the fact that even

those substances of the same crystal form as the yellow iodide of mercury, such as calc-spar, siderite, and hematite, are insoluble in naphthalene, and therefore probably incapable of acting as true isomorphous substances on the solution of the yellow iodide of mercury. However this may be, the fact remains that the yellow iodide of mercury and not the red variety of this compound precipitates the yellow iodide from supersaturated solutions of mercuric iodide in naphthalene, and it is further interesting to note that the yellow iodide is the only form of the compound ever precipitated from its supersaturated solutions by any substance. Either the yellow iodide is thrown out of these supersaturated solutions or nothing at all. These facts, therefore, strongly support the conclusion already advanced in the former communication on this subject, *viz.*, that solutions of mercuric iodide really contain the yellow modification of this compound and not simply molecules of the iodide, HgI_2, which may arrange themselves in the yellow or red form of the compound according to the nature of the crystal which is first presented to them.[1] It would seem, therefore, that red mercuric iodide changes to yellow in the act of passing into solution. In this connection it has been observed repeatedly that the yellow iodide seems to dissolve more readily and rapidly in organic solvents than the red. In order to determine whether such was really the case the rate of solution of the yellow and red iodide was tried in naphthalene, in the following manner :

Two portions of naphthalene, of 15 grams each, were weighed out and put into two glass-stoppered bottles of the same size and shape. These two bottles were clamped firmly together and placed in a bath of boiling water. Two equal portions of mercuric iodide were then weighed out, the quantity taken being in excess of that which 15 grams of naphthalene would dissolve at 100° C. One of these portions was then gently heated so as to convert it into the yellow modification

[1] In this connection certain recent observations of Wegscheider and Kaufler on the allotropy of phosphorus are worthy of note. According to these observers a saturated solution of yellow phosphorus in carbon disulphide sown with red phosphorus shows no perceptible change, and, on lowering the temperature, yellow phosphorus separates. They have reached the conclusion, therefore, that these two forms of phosphorus are not polymorphous, but chemically different (Monatsh. Chem., **22**, 700-706 (1901)).

and then quickly cooled to the ordinary temperature again. The red portion of the iodide was then put into one of the bottles of naphthalene and the yellow portion into the other. Both bottles were then tightly stoppered and vigorously shaken for a short time, after which they were put back in the water-bath. After a few minutes the bottles were removed from the bath and 5 cc. of each of the solutions drawn out by means of a pipette, which had been heated to 100° C. These two portions of the solutions were then boiled with water and zinc dust and filtered and the amount of iodide in each determined volumetrically with N/10 silver nitrate. In this way 5 cc. of the solution that had been prepared from the red mercuric iodide was found to contain 0.124 gram of mercuric iodide, whereas 5 cc. of the solution that had been prepared from the yellow iodide was found to contain 0.158 gram of mercuric iodide. A second experiment, carried out exactly like the first, gave for the same amounts of solution the following numbers respectively ; *viz.*, 0.122 gram and 0.144 gram of mercuric iodide. It would seem, therefore, that the yellow mercuric iodide dissolves more rapidly in naphthalene than the red. The results are in harmony with the view already advanced in our former communication, *viz.*, that the red iodide is insoluble in these solvents and that in the act of solution it is changed to the yellow form of the compound, which then dissolves at once. The fact that the red iodide dissolves more slowly than the yellow is in support of this conclusion.

The Stability of the Yellow Mercuric Iodide under Different Solvents.

The stability of the yellow mercuric iodide varies greatly under different solvents. When crystallized from ethyl alcohol, acetone, benzene, toluene, ethyl iodide, ethylidene chloride, ethyl cyanide, and phenyl cyanide the yellow iodide thus obtained changes to red very rapidly under the solvent, whereas, when crystallized from amyl alcohol, allyl alcohol, naphthalene, isobutyl bromide, ethyl butyrate, methyl salicylate, and phenyl salicylate it changes to red very slowly under the solvent. That the solvent actually exerts some influence on the stability of the yellow iodide is seen from the fact that

the yellow iodide obtained by crystallization from ethyl iodide changes rapidly to red if allowed to remain under the solvent, whereas if removed from the solvent and dried in the air it is only slowly changed to red. In one batch of crystals thus prepared and allowed to stand in the air a number of yellow ones were found after two and a half days. On the other hand, under ethyl butyrate the yellow iodide is very stable, whereas the same crystals, when exposed to air and not in contact with the solvent, were found to alter very rapidly. There are doubtless many peculiarities connected with the action of various solvents on the labile form of this compound which as yet cannot be satisfactorily explained. On the other hand, in studying the stability of the yellow iodide under different solvents, it soon occurred to us that its stability under the solvent increases with the viscosity of the latter. That such is the case is rendered evident by a comparison of its stability under ethyl and amyl alcohol, benzene, and naphthalene, respectively. It was also observed that light accelerates the change of the yellow iodide into the red, under all solvents. It therefore occurred to us that the yellow iodide could be preserved unchanged for a considerable time provided it were crystallized from a very viscous solvent and kept in the dark. The following experiments were therefore tried in order to determine whether such was really the case : Very concentrated solutions of mercuric iodide in glycerin were prepared by heating the iodide in glycerin to 200° C. in perfectly clean test-tubes. On cooling, these solutions deposited very minute crystals of the yellow iodide. The tubes were then placed in the dark room. The first tube thus prepared showed no trace of the red compound until one week after it had been made. At the end of two weeks the red iodide was pretty well diffused throughout the tube. Another tube prepared in exactly the same way showed no trace of the red compound for two weeks, and at the end of five weeks there was only a thin layer of red crystals on the surface of the yellow ones. Two tubes of the yellow iodide in glycerin were then prepared by pouring a hot solution of the iodide in glycerin into cold glycerin. In this way the yellow iodide was precipitated in even smaller crystals than by crystallizing

from the hot solution. These tubes remained unchanged for two weeks, at the end of which time crystals of the red iodide were seen diffused throughout the mass of the yellow compound. It was thought that possibly the friction of the yellow crystals against the walls of the test-tube might have caused the change of the yellow to red. In order to do away with this, if possible, a solution of the iodide in glycerin, containing the fine yellow crystals in suspension, was poured into small cups made of paraffin. Under these conditions the yellow iodide remained unchanged for two weeks, at the end of which time red crystals began to make their appearance. It will be observed, therefore, that the paraffin vessels offered no particular advantage over the test-tubes.

The next solvent tried was a very thick, concentrated solution of cane-sugar. Under this solvent the yellow iodide remained unchanged for several days, after which the mass of yellow crystals gradually became red. In this connection it should be observed that under water the yellow iodide of mercury is very unstable, so that the cane-sugar, by increasing the viscosity of the solution, greatly increases the stability of the yellow iodide.

The conduct of the yellow iodide under vaseline was next studied. Mercuric iodide was dissolved in boiling vaseline and the solution allowed to cool. The yellow iodide separated on cooling and the vaseline became gelatinous. One tube prepared in this manner and placed in the dark room showed absolutely no trace of red at the end of nine weeks. At the end of this time a few of the yellow crystals turned red, but even now, one year and seven months since this tube was prepared, probably not more than 25 per cent of the yellow crystals have changed to red. Another tube containing the yellow iodide and vaseline was prepared on the 14th of April, 1900. To-day, Nov. 12, 1901, this tube shows no red crystals except in the upper part of it, where a little of the solution stuck to the walls of the tube when it was poured in. Otherwise the yellow iodide under the vaseline remains unchanged and is as pure yellow now as it was the day that it was put in the tube. Yellow mercuric iodide is more stable in contact with vaseline than any solvent thus far studied.

The fact that the yellow iodide is more stable in contact with viscous solvents than with those that are very mobile is in harmony with the general conduct of these two classes of solvents and can, therefore, be readily explained.   In viscous solvents all chemical and physical changes are slow, sudden changes of temperature are practically impossible, and the motion and rubbing of suspended particles but slight.   When these facts are kept in mind and we consider also the general reluctance on the part of all substances to form new phases, we can readily understand why the yellow mercuric iodide resists alteration in viscous solvents.

STATE COLLEGE OF KENTUCKY,
     LEXINGTON, Nov., 1901.

XCI.—ON BENZOYLBENZYLUREA, BENZOYLPARA-TOLYLUREA AND THE CORRESPONDING PSEUDOETHYLUREAS: A CORRECTION.

BY HENRY L. WHEELER AND TREAT B. JOHNSON.

In our article on the behavior of acylthioncarbamic esters with alkyl iodides and amines[1] we described products obtained by the action of benzylamine and paratoluidine on ethyl benzoylthioncarbamate, which, from our analytical data, were concluded to be benzoylbenzyl and benzoylparatolylurea.

The compounds melted at 89° and 80°, respectively.   The fact that these are abnormally low melting-points for benzoylureas escaped our notice until recently, whereupon, on making a reexamination of the products, it was found that they are not normal but pseudoureas.

Pure benzoylpseudoethylparatolylurea,

$$C_6H_5CON = C(OC_2H_5)NHC_6H_4CH_3,$$

prepared from ethyl benzoylimidothiocarbonate boiling at 104° at 16 mm. pressure, is a solid that can be repeatedly recrystallized from strong alcohol, and it melts sharply at 75°. When this is treated with dilute hydrochloric acid, ethyl chloride is evolved and the material is smoothly transformed into

[1] This JOURNAL, **24**, 208, 209 (1900).

benzoylparatolylurea, melting at 222° to 223° and not at 80°.

Some of the original material melting at 89° which was described as benzoylbenzylurea, when treated with hydrochloric acid, also evolved ethyl chloride and passed smoothly into the true benzoylbenzylurea, melting at 165° to 166°.

These amines, like ammonia, therefore react on ethyl benzoylthioncarbamate with evolution of hydrogen sulphide and formation of pseudoureas as follows:

$$C_6H_5CONHCSOC_2H_5 \longrightarrow C_6H_5CONH(HS)C(NHR)OC_2H_5 \longrightarrow$$
$$C_6H_5CON=C(NHR)OC_2H_5.$$
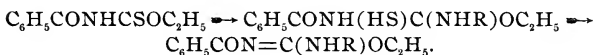
Benzoylpseudoethylparatolylurea crystallizes from alcohol in colorless, small, flattened prisms melting at 75°.

	Calculated for $C_{17}H_{18}O_2N_2$.	Found.
N	9.92	10.1

Benzoylparatolylurea, from the above and hydrochloric acid, crystallizes from alcohol, in which it is difficultly soluble, in the form of needles, melting at 222° to 223°.

	Calculated for $C_{15}H_{14}O_2N_2$.	Found.
N	11.02	10.87

Benzoylpseudoethylbenzylurea forms colorless, flattened prisms or plates from alcohol, melting at 89° to 90°.

	Calculated for $C_{17}H_{18}O_2N_2$.	Found.
N	9.92	10.03

Benzoylbenzylurea forms colorless prisms from alcohol, melting at 165° to 166°.

	Calculated for $C_{15}H_{14}O_2N_2$.	Found.
N	11.02	11.28

NEW HAVEN, CONN.,
Feb. 4, 1902.

REPORTS.

The Molecular Weight of Sulphur.

That at high temperatures sulphur vapor exists as the molecule S_2 has never been doubted since the work of Troost,[1] Bineau,[2] and of V. and C. Meyer.[3] Especially has the work of Victor Meyer alone and in company with Biltz[4] established the existence and constancy of this molecule, S_2, between the temperatures 900° and 1700° C.

For a long time also, based upon the measurements made by Dumas,[5] Mitscherlich,[6] and V. and C. Meyer,[7] the density of sulphur vapor at temperatures between 490° and 530° was placed at about 6.6. The mean of the various determinations are :

Dumas	6.64
Mitscherlich	6.57
V. and C. Meyer	6.63

These lead to a molecular weight of 192. That is the sulphur molecule exists as S_6.

The first to cast doubt on the existence of the six-atom molecule was Biltz,[8] in 1888, although Liebig, previous to 1840, had determined the molecular weight of sulphur by Dumas' method but had found such large differences in his values that he had never published them. This fact remained unknown until after the publication of the correspondence of Liebig and Berzelius.

Biltz determined the density of sulphur vapor at various temperatures between 468° and 606° by both the Dumas and the Victor Meyer method. Most of his determinations were made at 518° and 606°, using the vapor of phosphorus pentasulphide, and zinc chloride as the heating agents. Between 468° and 606° the vapor was found to vary in density from 7.3 to 3.5 by the Victor Meyer method, and between 7.8 and 4.7 by the Dumas method.

The values obtained by the method of V. Meyer were always lower than those obtained by the Dumas method at the same temperature. These discrepancies Biltz explains as due to the nitrogen used as the gas to be displaced in the Victor

[1] Ann. chim. phys., [3], **58**, 257.
[2] *Ibid.*, [3], **59**, 456.
[3] Ber. d. chem. Ges., **12**, 1115.
[4] Ztschr. phys. Chem., **4**, 266.
[5] Ann. chim. phys., **50**, 178; Pogg. Ann., **21**, 559.
[6] Pogg. Ann., **29**, 217.
[7] Ber. d. chem. Ges., **11**, 2259.
[8] *Ibid.*, **21**, 2013 ; Ztschr. phys. Chem., **2**, 920.

Meyer method. He found that when the quantity of sulphur used in his experiments was increased, and when precautions were taken to prevent the rapid diffusion of the sulphur vapor into the nitrogen, the density approached more nearly to that obtained by the Dumas method.

As the result of his work, Biltz concluded that there was no ground for the assumption of the existence of the molecules S_6, S_8, or S_{10}, and that the increase in density observed as the temperature of the experiment was lowered was not due to an association of the simpler molecules, but that at the lower temperatures the deviations from the gas laws shown by the vapor were very much greater than at higher temperatures. He also concluded that the density corresponding to the molecule S_2 was the only one which remained constant over any considerable range of temperature.

Biltz's conclusion that he had proved the non-existence of the molecule S_6 was soon challenged. Ramsay[1] pointed out that Biltz's results had not proved, to him at least, the non-existence of a sulphur molecule containing 6 atoms.

Biltz,[2] in reply, admitted the possibility of the molecule S_8, but stated that he had not worked over a sufficiently large range of temperature to prove its existence. The existence of the molecule S_6 he would not admit.

Riecke[3] used Biltz's results as a groundwork to deduce a law governing dissociation by steps, as well as to show mathematically that the sulphur molecule passes from S_8 to S_2 with the intermediate formation of the molecule S_6 according to the equation

$$S_8 = S_6 + S_2;$$
$$S_6 = 3S_2.$$
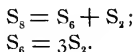
Nernst[4] and Ostwald,[5] in their text-books, have also emphasized the fact that the non-existence of the molecule S_6 had not been proved.

C. Schall,[6] using a method devised by himself for measuring densities under diminished pressure, and hence, at lower temperatures, gives the value S_8, and concludes with Biltz that the molecule S_6 is non-existent.

Krause and V. Meyer[7] have also given the value S_8 at temperatures below the boiling-point of sulphur under atmospheric pressure. Neuberg[8] has also arrived at the same conclusion.

[1] Ztschr. phys. Chem., **3**, 67.
[2] *Ibid.*, **3**, 228.
[3] *Ibid.*, **6**, 430.
[4] " Lehrbuch der allgemeinen Chemie," 2nd Ed., Vol. I., p. 2188.
[5] " Theoretische Chemie," 2nd Ed., p. 415.
[6] Ber. d. chem. Ges., **23**, 919, 1701 (1890).
[7] Ztschr. phys. Chem., **6**, 5 (1890).
[8] Ber. d. chem. Ges., **24**, 2544 (1890).

Paterno and Nasini[1] were the first to determine the molecular weight of sulphur in solution by the cryoscopic method. They thought that they had established the existence of the molecule S_6 in benzene as a solvent.

Beckmann,[2] using carbon bisulphide as a solvent, made it very probable that the molecule S_8 does exist, although he could not with certainty exclude the existence of S_9.

Hertz,[3] using naphthalene, obtained a value S_8 for the molecule. By the boiling-point method, Helff,[4] with carbon bisulphide as a solvent, reached the same conclusion as Beckmann.

Sakurai[5] and Biltz,[6] using nitrobenzene, obtained a molecular weight between S_7 and S_8. Later Orndorff and Terasse,[7] in boiling naphthalene, xylene, and phenetol, and in freezing diphenyl, found the value S_8, but in freezing naphthalene the value S_7, while in sulphur monochloride they obtained S_2, and in boiling toluene and carbon bisulphide found the molecule S_9.

Gloss[8] has given for the different modifications of sulphur values between S_8 and S_9, working with naphthalene by the freezing-point method.

Barnes,[9] working in carbon bisulphide, has obtained the value S_8.

The work of Orndorff and Terasse has been completely contradicted by Aronstein and Meihuizen,[10] who worked with solutions in toluene, xylene, naphthalene, and carbon bisulphide, both above and below the transition-point of rhombic to monoclinic sulphur, and above and below its melting-point. They obtained a constant value S_8.

It seems, then, to be settled that at high temperatures sulphur exists as S_2, while at low temperatures and in solution it exists as the molecule S_8. But this question still remains to be settled : How does the molecule S_8 break down ? Does it pass at once to the molecule S_2 or do we have an intermediate formation of S_6, as has been generally accepted ?

In the last year or two, two important papers bearing on this point have appeared.

Bleier and Kohn[11] have used in their experiments a modification of the method of Victor Meyer, in which, instead of measuring the volume of gas displaced by the substance whose

[1] Ber. d. chem. Ges., **21**, 2153 (1888).
[2] Ztschr. phys. Chem., **5**, 76 (1890).
[3] *Ibid.*, **6**, 358.
[4] *Ibid.*, **12**, 200.
[5] J. Chem. Soc., 1892, 989–1002.
[6] Ztschr. phys. Chem., **19**, 425.
[7] This JOURNAL, **18**, 173.
[8] J. Phys. Chem., **2**, 451.
[9] *Ibid.*, **3**, 151.
[10] Verh. der Königl. Akad. Wiss., Amsterdam, July, 1898; Centrbl., (1898), II., 1194; (1900), I., 392.
[11] Monatsh. Chem., **20**, 505, 909 ; **21**, 575.

vapor-density is to be measured, they have measured the change in pressure produced when the apparatus is connected with a manometer.

Their calculations are based on the gas law that equal numbers of gram-molecular weights of various substances, when in the gaseous state, produce equal changes in pressure under similar conditions of temperature and volume.

The above manner of stating the underlying gas laws is similar to the Van 't Hoff law of osmotic pressure, which forms the foundation of the Raoult-Beckmann method of determining molecular weights.

They use this gas law to determine the molecular weights of substances when vaporized, as the Van 't Hoff law is applied to solutions for determining the molecular weight of substances in solution. The pressure change produced by the milligram-molecular weight of any substance when vaporized in the apparatus at a known temperature is called the constant of the apparatus for this temperature. Hence :

$$q : p = m : c \, ;$$

or

$$m = \frac{qc}{p},$$

where m is the molecular weight of the substance to be determined.

q is the weight of the substance vaporized in the apparatus.
c is the constant as explained above.
p is the change in pressure observed when q is vaporized.

The following cut shows their apparatus as used in the determination of the molecular weight of sulphur.

A is the vessel in which the substance is vaporized. B is the manometer. The arms communicate with one another both below and above as long as this last communication is not broken by the closing of b. The manometer is filled with a paraffin oil of high boiling-point (400° to 500°), whose specific gravity is between 0.7 and 0.8. Hence a difference of pressure equivalent to 2 mm. of mercury would show on this manometer a difference in level of 35 mm. The length of the manometer arms is sufficient to show a change in pressure of 400 mm., which is equivalent to 24 mm. of mercury. C is a vacuum reservoir closed by a ground-glass stopper with three openings. c and d are stop-cocks, c being a three-way cock containing a very fine hole for the admission of air to the apparatus. e is a small mercury manometer. a connects with an air-pump.

In carrying out a determination, the substance is suspended
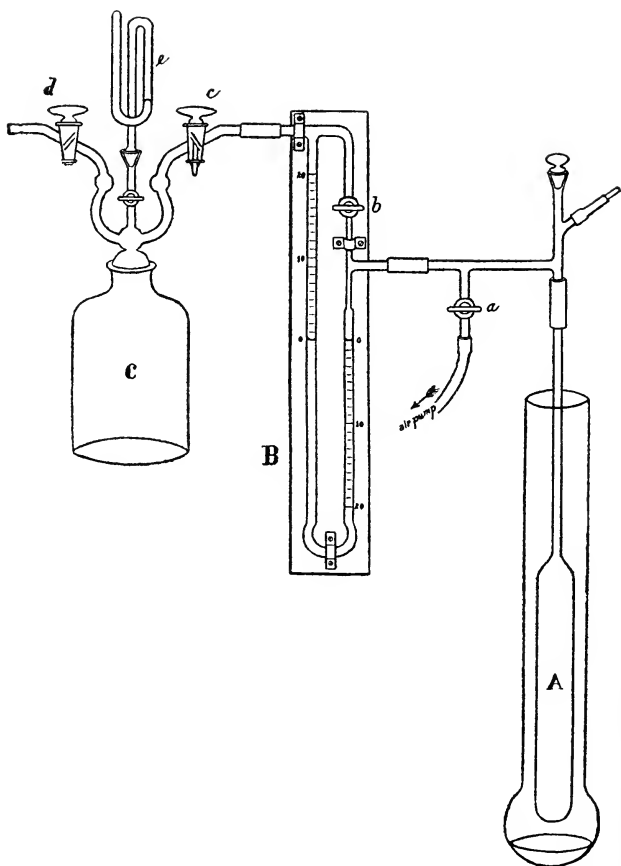
in a small tube at *f.* The stop-cock *b* being open, the whole apparatus is pumped out to the desired pressure, while the liquid in the jacket surrounding A is boiled. The stop-cock *b* is then closed. The substance is allowed to drop to the bottom of A, when it is vaporized. As soon as the manometer becomes constant the difference in the level in the two arms is read. This gives the necessary data for the calculation of *p*, and, hence, of *m*, the molecular weight.

Using this method, Bleier and Kohn have established the dissociation isothermals of sulphur vapor over considerable ranges of pressure, at the temperature of boiling diphenylamine (310°), amyl benzoate (262°), quinoline (236°), ethyl benzoate (214°), and dimethylaniline (192°).

The density of the sulphur-vapor increases regularly with increase in pressure. The following table shows the least and greatest densities obtained at the various temperatures:

Temperature.	Pressure in mm. of mercury.	Density. $O_2 = 1.$
310°	42.5	7.43
310°	1.6	5.80
262°	18.4	7.49
262°	1.5	6.66
236°	9.4	7.66
236°	1.4	6.92
214°	4.2	7.80
214°	1.2	7.20
192°	2.1	7.85
192°	0.9	7.48

From their results, and from the curves which they have plotted from these results, it is seen that the values for the densities gradually approach the value 8, and in the pressure-density curve become asymptotic to this value. From this they conclude that the undissociated sulphur molecule is S_8.

If the molecule S_6 exists, as Riecke had concluded from a theoretical consideration of Biltz's results, as has already been mentioned, it would be expected that the density 6 would be found to remain constant over a considerable range of pressure. In the results obtained at 310°, the only temperature at which densities were found lower than 6, no trace of any such constant value was observed and the curves show no tendency to depart from their regular form. These results would point to the non-existence of the molecule S_6, but Bleier and Kohn conclude that, to settle this point definitely, dissociation isothermals at higher temperatures are necessary as well as to

obtain densities lower than 5.80, the lowest obtainable at the highest temperature at which they worked.

Biltz and Preuner[1] have completed the proof necessary to completely exclude the molecule S_6 by a series of experiments, using the Dumas method under diminished pressure.

The principle of their apparatus is in general that of Habermann,[2] but special modifications have been introduced to meet the difficulties of their experiments. Their determinations were made at the temperature of sulphur boiling under atmospheric pressure, and at pressures varying between 14.0 and 539.2 mm. of mercury.

The greatest care and a high degree of accuracy are shown in the work. The sulphur used was subjected to five distillations before use. As the quantity used in an experiment was very small, especially under the lower pressures, analytical methods for determining the amount of sulphur in the Dumas bulb were employed in order to avoid the errors due to weighing very small amounts. In all, thirty-two determinations were made which show a gradual rise in density with increase in pressure. No evidence of the existence of the six-atom molecule was found, as is seen by a study of the following curve. Not the slightest tendency for the curve to straighten out or show irregularities is noticed in the neighborhood of density 6.

Pressure in millimeters of mercury.
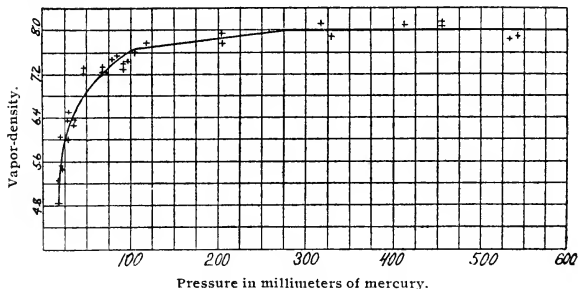
In conclusion, it has been shown that at the lowest temperatures at which sulphur can be vaporized it exists as S_8. As the temperature rises, this commences to break down into the molecules of S_2, while at temperatures above 900° sulphur exists solely as S_2. In solutions it exists as S_8.

CHARLES F. LINDSAY.

[1] Monatsh. Chem., **22**, 627; Ber. d. chem. Ges., **43**, 2490; Ztschr. phys. Chem., **34**, 323.
[2] Ann. Chem. (Liebig), **187**, 341 (1877).

Sulphuric Acid and Its Preparation by the Contact Method.

Since the announcement made several years ago that a successful catalytic method for the preparation of sulphuric acid in large quantities was in use at the Badische Anilin- und Soda-Fabrik, chemists have been anxious to obtain all the information possible regarding the process. The German Chemical Society could not have selected a better person to speak on this subject than R. Knietsch, who is connected with the Badische Anilin- und Soda-Fabrik, and who has taken an active part in the successful application of the method. In a very interesting lecture[1] delivered at the Hofmann-House, Oct. 19, 1901, he sketched the story of the solution of the problem and furnished valuable additions to our knowledge of sulphuric acid.

After referring to the important rôle that the acid has always played in inorganic chemistry and its growing importance in the domain of organic chemistry, owing to its extensive use in the manufacture of alizarin and synthetical indigo, he pointed out the extreme theoretical simplicity of the reaction when oxygen and sulphur dioxide combine, a reaction which, however, is very slow and requires the assistance of a catalytic agent. In the old method a gaseous agent was used and a dilute acid was obtained, but in the improved method a solid, practically permanent, agent is used and solid sulphur trioxide is obtained. In studying the historical development of the subject four periods can be recognized.

The first period began with the discovery, made by Peregrine Phillips, Jr., of Bristol, who took out an English patent in 1831, of the catalytic action of platinum in the formation of sulphuric acid. Humphry Davy had discovered the catalytic action of platinum as early as 1817, and had studied its action on a mixture of oxygen or air with hydrogen, carbon monoxide, ethylene, and other gases; but neither he nor Döbereiner applied it in the preparation of sulphuric acid.

Seventeen years after Phillips' discovery Schneider, a Belgian chemist, supposed that in the discovery of the catalytic action of pumice stone the problem had been solved; but his great expectations were not realized. In 1846 a patent was issued to Jullion for the use of platinum asbestos as a catalytic agent, but it was not until later, and by others than the discoverer, that it was used in the preparation of sulphuric acid.

The second period was marked by the discovery made by Wöhler and Mahla that the oxides of copper, iron, and chromium also act as catalytic agents. They found that the oxides

[1] Ber. d. chem. Ges., **34**, 4069.

of copper and iron, in the absence of oxygen, were reduced by the sulphurous acid with the formation of sulphuric acid, the latter being formed as long as there was any oxide to oxidize the sulphurous acid, while with the oxide of chromium, which was not reduced, no sulphuric acid was formed unless oxygen was present. These and similar experiments enabled them to explain the phenomena and formed the basis of the later work of Lunge and that described in this paper. A number of patents were granted during this period for the use of a variety of substances as catalytic agents, but fuming sulphuric acid could not be made, by any of these methods, at a price which would enable it to compete with that made by the distillation of iron sulphate.

We come now to the turning-point, to the work of Clemens Winkler. As a result of experiments, Winkler concluded that only a stoichiometrical mixture of two volumes of sulphurous acid and one volume of oxygen would form sulphuric acid, and that the presence of any other gas, even an excess of oxygen, would retard and decrease the action. He obtained the necessary mixture by heating sulphuric acid, forming water, oxygen, and sulphur dioxide, and condensing the water. The oxygen and sulphur dioxide, in the presence of the contact mass, unite to form sulphur trioxide. This work was of great importance and led to the manufacture of the fuming acid by a method which could compete with the ferrous sulphate method, which had had a monopoly of the field. Ten years later a process was devised for the use of air instead of pure oxygen, the retarding influence of the nitrogen being overcome by carrying on the action under pressure. None of these methods, however, enabled them to use the furnace gases or to compete with the chamber process for making dilute acid. Although it was considered impossible to use the furnace gases, the great importance of a cheap method for the manufacture of the pure acid led the Badische Anilin- und Soda-Fabrik to undertake a thorough investigation of the subject. As the residual gases in the chamber process contain 6 per cent of oxygen by volume, and as the furnace gases, after being in contact with the contact mass, also contain an excess of oxygen, it was difficult to understand why there was an incomplete formation of acid. Experiments made on the small scale with pure gases showed that with even strongly diluted gases the yield was almost quantitative and the dilution, if anything, increased the yield.

This observation disproved the results of Winkler regarding the retarding action of diluting gases and led to an exhaustive study of the conditions influencing the reaction.

The same experiments were carried out with the natural fur-
nace gases, which were conducted into the laboratory through
long lead pipes. These pipes served the purpose of collecting
the solid particles. After the gases had passed through
several vessels of sulphuric acid, they were brought in con-
tact with the catalytic agent, and an excellent yield of acid
was obtained, the mass seeming to retain its full power even
after several days. When similar experiments were made on
the large scale, however, the contact mass rapidly became in-
active, even though the gases, in addition to being subjected
to other methods of purification, were filtered through coke
and asbestos filters, and were as pure as is possible on the
large scale. An examination of the furnace gases showed
that, while the action on the contact mass was due partly to
the presence of antimony, bismuth, lead, zinc, and other sub-
stances in small quantities, the most injurious substance
was arsenic, which was able, when present only to the extent
of 1 to 2 per cent, to poison the mass and render it entirely inac-
tive. The removal of the small amount of arsenic trioxide
present in the gases as a mist was a problem which had been
studied by many chemists, but had never been successfully
solved.

After the expenditure of an immense amount of time,
patience, and money a method was devised by which, through
cooling and washing and other processes, the exact details of
which are not given, the gases were *absolutely* freed of all im-
purities, especially those in the solid condition. It was found
that the ease with which the solid particles could be precipi-
tated depended largely upon the rate of cooling, slow cooling
greatly facilitating it. Although it was supposed that acid of
a concentration of 90 per cent would not act on iron, or, if so,
would form sulphur dioxide, the decrease in power of the con-
tact mass, which only began to appear after weeks or months,
was shown to be due to the formation of hydrogen from the
iron and sulphuric acid and the action of this on an arsenic
compound to form arsine. Even the trace of arsenic con-
tained in the small amount of sulphur, which passed through
unprecipitated, was sufficient to injure the contact mass. But
this was easily removed, as was also the sulphuric acid which
was formed in the furnace and which before had acted on the
iron and the arsenic compounds, by spraying the gases after
they issued from the furnace where the pyrite was burned.

In the technical preparation of the fuming acid very little
attention had been paid to the heat evolved when sulphur di-
oxide and oxygen combine, although it amounted to 22,600
cal. It was shown that the commonly accepted idea of the

necessity of heating the contact mass very high, in order to produce the combination when the diluted furnace gases were used, was incorrect, and that both the yield and the life of the mass could be increased if the tubes containing it were cooled in order to carry off some of the heat generated in the chemical combination of the two gases. A form of furnace was devised, something like a tubular boiler placed on end, and the contact mass arranged in the upright tubes of the furnace in such a way that the pressure and amount of surface of the mass exposed in each tube was the same. Under these conditions the process is a continuous one and the mass retains its full power for a year or more.

The ordinary method of absorbing gases by passing through a series of vessels containing water or dilute acid, would not entirely remove the sulphur trioxide even when a number of the absorbing flasks were used; but one vessel containing acid of 97 to 98 per cent sulphuric acid absorbs it instantly and entirely.

In order to keep the concentration at this point the excess of sulphur trioxide is removed from time to time or water is added. By the method just described the experimenters were able to obtain acid of any concentration and mixtures of the acid and sulphur trioxide in all proportions. A careful study of the properties of acids of different concentration showed not only interesting facts regarding the variations of the same property with acid of different strength, but also that the dif-

1 ——— Melting-point curve.
2 - - - - Boiling-point curve.
3 -·-·- Vapor-tension at 100°.
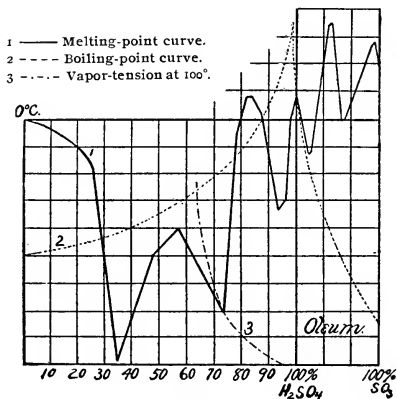
Fig. I.

ferent properties of the acid of the same concentration varied in the same way. In order to show the results in a clear manner they have been plotted in curves.

An examination of the curve representing the boiling-point (Fig. I., 2) will show that it increases from both sides until a
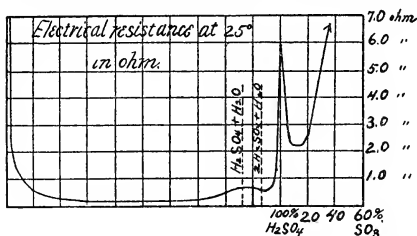
Fig. II.

maximum is reached in an acid of $98\frac{1}{3}$ per cent. Starting with a more dilute acid and heating the solution, there is a loss of water until the concentration reaches that of the acid just referred to, after which the rest of the acid distils over at a constant pressure and as a definite substance, while, starting with a more concentrated acid, there is a loss of sulphur trioxide until the same concentration is reached as before, when the same results are obtained.

The curve representing the vapor-pressure (Fig. I., 3) diminishes gradually and reaches a value of zero at a point corresponding to the $98\frac{1}{3}$ per cent acid. The electrical resistance (Fig. II.) begins to increase very rapidly when the $98\frac{1}{3}$ per cent acid is reached, after having reached a maximum at a point corresponding to a compound of the formula $H_2SO_4 + H_2O$. It then decreases and finally ascends rapidly. Although cast-iron is not readily attacked by concentrated sulphuric acid, the oleums (the term used for the mixtures of the acid and sulphur trioxide) sink into the pores of the iron and generate there sulphur dioxide, hydrogen sulphide, and carbon dioxide from the carbon in the iron. The critical temperatures of these gases are low, and under these conditions the pressure sometimes becomes sufficient to cause explosions. Wrought iron (Fig. III.), on the other hand, which is attacked by concentrated sulphuric acid and even by the oleums of 10 to 15 per cent is not acted on at all by oleum containing more than 27 per cent sulphur trioxide. Weber has shown that pure sulphur trioxide melts at $17°.7$. If now water is slowly added, the melting-point will rise until with an acid

containing 85 per cent sulphur trioxide a maximum is reached
at 27° (Fig. I., 1). This applies, however, only to freshly
prepared specimens as, after standing, they polymerize and no
longer melt, but sublime at a higher temperature. With
further dilution it reaches, with an acid containing 60 to 65
per cent of the trioxide, a melting-point of 0° to 2°, and, rising
again, reaches a maximum at 36°, the acid corresponding to
the formula $H_2SO_4 + SO_3$. This point is of special interest,
as it coincides with the point of greatest pressure, the greatest
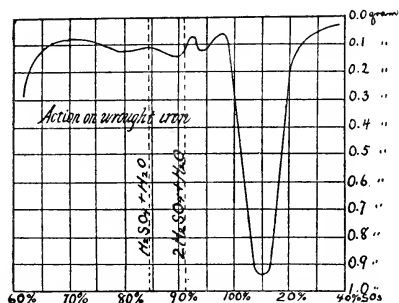
Fig. III.

viscosity, and a break in the curve of capillarity. With
further dilution we find at −12° an acid which will attack the
iron, at +10° one represented corresponding to the monohy-
drate, at −35° the acid $2H_2SO_4 + H_2O$, and at +8° the acid
$H_2SO_4 + H_2O$.

The author also showed the results obtained from a study
of the specific heat, heat of solution, capillary rise, and vis-
cosity of acids of all concentrations. In the case of the vis-
cosity, which increases as the concentration of the acid in-
creases, until an acid containing 50 per cent oleum is reached,
when it begins to decrease again ; the values for water and
pure sulphur trioxide were found to be identical.

Furnace gases which contained, besides nitrogen, a stoichio-
metrical mixture of oxygen and sulphur trioxide, when brought
in contact with the catalytic mass at different temperatures
and at different rates of flow, never gave more than 77 to 91
per cent of the theoretical yield ; but, if one of the gases was
present in excess, the other was completely removed. The
curves S and S' in Fig. IV. represent the results with the
stoichiometrical mixture.

The technical furnace gases formed by the roasting of pyrites contain about 7 volumes of sulphur dioxide, 10 volumes of oxygen, and 83 volumes of nitrogen. If this mixture is passed through an empty porcelain tube there is a small
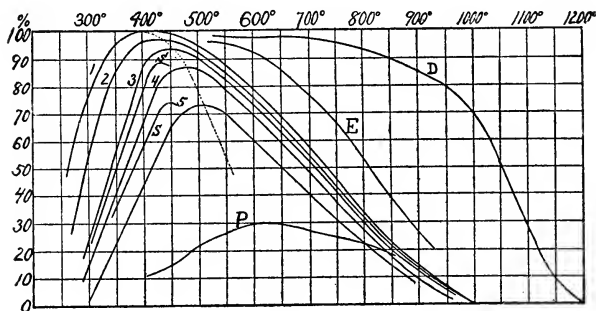
Fig. IV.

yield of acid (Fig. IV., *P*), but if a contact mass, as platinum asbestos, is placed in the tube, even at 200° the gases begin to combine, the yield increasing up to 400°–430°, where 98 to 99 per cent of the theoretical yield is obtained. As the temperature rises higher the acid is decomposed, the yield at 700° to 750° being only 60 per cent and at 900° to 1000° becoming practically zero.

If the amount of contact mass is diminished or, what is the same thing, the rate of flow increased the results represented in curves 1, 2, 3, 4, and 5 were obtained. While these are in general parallel they still show a tendency to diverge as they approach the point of maximum yield and then approach one another, reaching the zero point at about 900° to 1000°. As the rate of flow increases not only does the yield decrease, but the temperature at which the maximum yield is obtained becomes greater, as is indicated by the dotted line. Experiments with empty tubes through which the sulphur trioxide was passed showed that, in the absence of finely divided solid matter, the sulphur trioxide was very stable and was not finally decomposed until a temperature of 1200° was reached (curve *D*). If, however, the tube was filled with any solid matter the substance was decomposed at a lower temperature as shown by curve *E*.

If the results obtained in such a process are plotted as in Fig. V., we can, by reference to the chart, determine what amount of contact mass will give the best yield at any given

Contact mass or time.
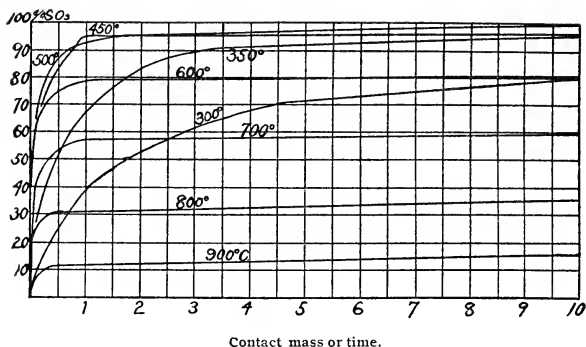
Fig. V.

temperature. The regions below 200° and above 900° to 1000° can be regarded as reactionless, while the best yield is obtained between 200° and 450°. Although the amount of product formed is not directly dependent upon the nature of the contact mass, yet the latter must be one which will give the greatest efficiency at about 450°. All substances which reach their highest efficiency above this temperature will never cause a quantitative yield, no matter how long the gases may be kept in contact, as they will be partly regenerated if they have first combined. The only substance which fulfils these conditions is platinum, even members of the same family not showing an equal efficiency. The introduction of this method has enabled the Badische Anilin- und Soda-Fabrik to increase the yield of the anhydride from 18,500 tons in 1888 to 116,000 tons in 1900.

At the close of the paper the author calls attention to the fact that such a piece of work could not have been carried out by an individual. It required the immense resources of such a company as the Badische Anilin- und Soda-Fabrik, directed by the far-reaching knowledge of Heinrich Brünck, the experience of Gustav Jacobsen, and the valuable aid of ingenious mechanics to carry it to success.   J. Elliott Gilpin.

REVIEWS.

An Introduction to Chemical Analysis for Students of Medicine, Pharmacy, and Dentistry. By Elbert W. Rockwood, M.A., M.D., Professor of Chemistry and Toxicology in the College of Medicine, University of Iowa. Philadelphia : P. Blakiston's Son & Co. 1901.

This manual contains the regular course in qualitative inorganic analysis, tests for the common organic compounds including drugs and alkaloids, a section on volumetric analysis, chapters on the sanitary examination of water, the detection of poisons, and blowpipe analysis.

The book is well written ; it is simple, clear, and explicit. Particular attention is called to the reactions of substances used as drugs. Pages of questions inserted at the end of the chapters emphasize reactions bearing on medicine or pharmacy and serve for self-examination.

Prof. Rockwood's manual is brief enough to be studied in the time given to laboratory work in the average medical school, and yet contains a surprising amount of sound practice. E. R.

Kurze Anleitung zur Qualitativen Analyse. Von Dr. Ludwig Medicus, Professor an der Universität Würzburg. Elfte Auflage. Tübingen, 1901. H. Laupp'sche Buchhandlung. Broschirt, M. 2 ; gebunden, M. 2.80.

That this is the eleventh edition of Prof. Medicus' Anleitung shows that the book retains the popularity won at its first appearance in 1877. The most noticeable change in the new edition is the brief treatise on solutions, mass reactions and chemical reactions in the light of physical-chemical theory, and the introduction into the text of brief explanations of single reactions in this sense.

This work occupies a position between the very brief manuals and the large text-books like that of Fresenius. It is full enough for most students. It gives the Bunsen flame reactions, and the reactions of the rare elements. It is deservedly popular. E. R.

High-Temperature Measurements. By H. Le Chatelier, zugénieur en Chef du Corps des Mines, Professeur de Chimie Minerale au Collège de France, and O. Boudouard, Assistant, Collège de France. Translated by George K. Burgess, Instructor in Physics, University of Michigan. First edition, first thousand. New York : John Wiley & Sons ; London : Chapman & Hall, Limited. pp. 230. 1901.

Attention has been turned recently to the measurement of very low rather than very high temperatures. This is due to

the fact that the low-boiling substances such as oxygen, air, nitrogen, and hydrogen can be obtained in the liquid form in any quantity desired. The measurement of very high temperatures has, however, not been disregarded, as is shown by the appearance of a volume like the one in hand. The author takes up the gas pyrometer, the calorimetric pyrometer, the electrical resistance pyrometer, the thermoelectric pyrometer, the heat-radiation pyrometer, the luminous-radiation pyrometer, the contraction pyrometer, fusible cones, and recording pyrometers.

The importance of high-temperature measurements is obvious to any one who has followed the work of Moissan, Le Chatelier, and Roberts-Austen. By means of the electric furnace Moissan has opened up an entirely new field for inorganic chemistry, and it is highly desirable to know, at least approximately, the temperatures at which these transformations take place. Le Chatelier has studied the electrical resistance of metals at very high temperatures, also their dilatation and allotropic transformations. He has shown that many new compounds probably exist at the more elevated temperatures. A number of allotropic modifications of iron and other elements have also been shown to exist by the work of Roberts-Austen. The applications of these extremely high temperatures have proved of incalculable service also in the industries.

The work needs no other commendation than that it was written by Le Chatelier. The English of the translation could, however, have been easily improved.   H. C. J.

DIE NORMALELEMENTE UND IHRE ANWENDUNG IN DER ELEKTRISCHEN MESSTECHNIK. Von DR. W. JAEGER, Kaiserl. Professor, Mitglied der physikalisch-technischen Reichsanstalt in Charlottenburg. Verlag von Wilhelm Knapp, Halle A. S. pp. 131. 1902.

The information concerning normal elements is so scattered that it is often difficult to find what is desired. The problem is further complicated by the fact that such widely different results have been obtained with the same element by different experimenters. In the present volume we have the best that is known concerning this important class of cells.

The author takes up the theory of the normal element, discussing the relations between the intrinsic energy of the cell and its electromotive force, the dependence of the electromotive force upon the concentrations of the solutions, the temperature coefficient, and the osmotic theory of the normal element.

The several normal elements are then studied in detail. These include the following :

Daniell-Fleming element : $Zn - ZnSO_4 - CuSO_4 - Cu$.
Clark element : $Zn - ZnSO_4 - Hg_2SO_4 - Hg$.
Gouy element : $Zn - ZnSO_4 - HgO - Hg$.
Helmholtz-Ostwald element : $Zn - ZnCl_2 - Hg_2Cl_2 - Hg$.
Warren de la Rue element : $Zn - ZnCl_2 - AgCl - Ag$.
Weston element : $Cd - CdSO_4 - Hg_2SO_4 - Hg$.

The book concludes with a chapter on the measurement of the electromotive force of standard elements, and the use of such elements. The electromotive force of the Clark element as measured by the silver voltameter on the assumption that one ampere in a second separates from silver nitrate 0.001118 gram of silver is :

$$1.4328 - 0.00119 \, (t - 15°) - 0.000007 \, (t - 15°)^2 \text{ volt.}$$

The work comes from the best source in the world, *viz.*, the Reichsanstalt, and its author has contributed much to the subject upon which he is writing. It will certainly find its way into every laboratory where measurements of electromotive force are made.   H. C. J.

SMOKELESS POWDER, NITROCELLULOSE, AND THEORY OF THE CELLU-
LOSE MOLECULE. By JOHN B. BERNADOU, Lieutenant United States
Navy. New York : John Wiley & Sons, 1901. 12 mo. pp. viii +
200. Price, $2.50.

As stated in the preface, the author " For purposes of comparative study . . . . . has brought together in the present volume a series of papers, by various investigators, upon the composition of cellulose and the properties of explosives prepared therefrom. He has supplemented these with an account of experiments made by himself, and from the whole has drawn certain conclusions as to the possible ultimate chemical composition of cellulose and the nitrocelluloses."

A general idea of the contents of the book can be obtained from the table of contents : Chapter I., Origin, Nomenclature, and Definitions ; Chapter II., Earlier Views as to Nitrocellulose Composition and Constitution ; Chapter III., The Conception of Progression in Relation to Composition and Constitution ; Chapter IV., Solutions of Nitrocellulose, Theory of the Cellulose Molecule. In the appendices the author has included translations of papers by Vieille and Bruley on " The Nitration of Cotton," one by Mendeléeff on "Pyrocollodion Smokeless Powders," and a sketch of his own work on the development of smokeless powders.

On account of the uncertainty regarding the exact composition of cellulose and its nitro compounds great confusion has arisen from the use of the same name for different substances, or different names for the same substance. The author gives exact definitions of the terms used by different writers and a

table of the synonyms. In tracing the historical development of the subject he shows how the investigators have been led to the conclusion that the cellulose molecule is more complex than had formerly been supposed, and the general course which the search for satisfactory smokeless powders has taken. Vieille has obtained eight nitrocelluloses, by working under different conditions, which differ in their solubility and stability.

The author has drawn conclusions regarding the composition and structure of cellulose from the action of solvents on the nitrocelluloses. It has been pointed out that the reactions of cellulose, in the cuprammonium, thiocarbonate, and mercerization processes, lead to the conclusion that the hydroxyl groups exist in both acid and basic form and that the solubility of the substance in a mixture of ether and alcohol at ordinary temperatures, while it will not dissolve in one alone, except at very low temperatures, is due to the different ways in which the two solvents act upon the hydroxyl groups, one acting upon the basic and the other upon the acid hydroxyl groups. Acting upon this suggestion, the author shows how a type unit of cellulose, represented by the composition $C_6H_{10}O_5$, which has four free single carbon bonds, could be written, and how the more complex polymeric forms could be built up of combinations of different numbers of these units. There is no limit to the possible number of such combinations, and the author suggests that by this assumption the definite chemical composition of the cellular form in the plant structure can be accounted for. He says that "the molecule need not be limited in composition to the simplest collection of the *lowest possible* number of atoms capable of entering into combination, but may be built up from a very great number of the elemental particles taken together in their proper ratios. Such a molecule would increase in amplitude according to the number of elemental particles entering into its composition; and the thought therefore suggests itself that *progressive variations in the amplitude of the molecular ring is a characteristic of organic life*, or conversely, that we may seek for the beginnings of organic life—at least in plant life—in the polymerization of the carbohydrates." He points out how, by the suggested structure, the polymerization, nitration, mercerization, and colloidation can be explained. The papers in the appendices by Mendeléeff, Vieille, and the author, who have been instrumental in developing the smokeless powders in use in the navies and armies of Russia, France, and the United States, respectively, give the general nature of the experiments of these experts, and furnish a valuable summary of results which have been difficult to obtain on account of

the secrecy maintained by the governments regarding this general subject. The author of this book is an expert on the subject, who is well qualified to present the matter in the clear and interesting form in which we find it here. Mendeléeff studied the theoretical conditions, which a satisfactory powder must fulfil, as regards safety from detonation, development of minimum heat and maximum propulsive effect, formation of little residue and keeping qualities, and, after studying many substances, finally suggested the use of pyrocollodion, as most successfully fulfilling all the requirements. The same explosive was independently developed in this country, and further improved by the addition of an oxygen carrier, so that the decomposition was not instantaneous, but similar to the effect of a number of subcharges exploding in succession and thus gradually increasing the velocity of the shot. Vieille and Bruley studied, in detail, the conditions influencing the formation of different nitrocelluloses, and were able to control fairly well the production of any desired compound.

J. E. G.

OUTLINES OF ELECTROCHEMISTRY. By HARRY C. JONES. D. Van Nostrand Co. 1901.

The contents of this little work is already familiar to many readers, having appeared as a series of papers under the title "Selected Chapters in Electrochemistry," in the *Electrical Review*, 1901. The author has aimed to present to engineers and others unfamiliar with the recent advances in physical chemistry a general idea of the fundamental principles on which modern electrochemistry is based. Although the work makes no pretense of being a systematic treatise on electrochemistry, all of the most important phases of the subject are touched upon, as will be seen from a synopsis of the contents, which includes chapters on Osmotic Pressure, The Electrolytic Dissociation Theory and Some of Its Applications, Electrolysis, The Velocity of Ions, Electrical Conductivity and Electromotive Force of Elements.

The reader will find these matters presented in a necessarily brief but, on the whole, admirably clear manner. Numerous references are made and long quotations taken from other works by the author. The natural tendency in an elementary discussion to make light of difficulties is sometimes apparent, and in several places a lack of proper balance between important and unimportant subjects is felt. For example, only about a page and a half are devoted to the question of the quantitative transformation of chemical into electrical energy —a matter of the greatest practical importance—while three chapters are devoted to the calculation of electromotive forces,

even the mathematical theory of liquid cells being worked out in some detail. The modern theories of electrolysis could have been made clearer if discussed subsequent to potential differences at metal-liquid junctions. The book fills, however, a real need, and can be heartily recommended to the class of readers for whom it is intended. It is unfortunate that the publishers have not seen fit to give it a more attractive form. It is to be hoped that the awkward size and arrangement of the page may be corrected in a later edition.

H. M. GOODWIN.

ON THE COMPOSITION OF DUTCH BUTTER. By J. J. L. VAN RYN, Director to the Royal Agricultural Experiment Station at Maastricht. London. 1902.

Owing to the fact " that Dutch butter, the origin of which placed its genuineness and purity beyond doubt, has been wrongly declared by foreign chemists to be a mixture of butter and margarine," the Netherlands government undertook a careful study of the case, and especially the conditions in the latter months of the year, as the trouble seemed to arise at that time. A very careful and exhaustive study of the conditions was carried out, and it was found, as here reported, that the conditions of feeding and pasturing, or " stabling," had a marked influence on the results, and showed that analytical results which are generally considered evidence of adulteration, could be obtained from specimens of pure butter under certain conditions of feeding, etc.   J. E. G.

THE LABORATORY COMPANION TO FATS AND OILS INDUSTRIES. BY. J. LEWKOWITSCH, M.A., F.I.C. London : Macmillan & Co. 1901.

This book, by the author of the well-known work "Chemical Analysis of Oils, Fats and Waxes, Etc.," is almost exclusively devoted to tables which are of great value to any one working with fats and oils, as the information regarding these substances has been collected and tabulated in a very convenient form. The different values given in the literature have been carefully scrutinized and only the most reliable ones given.   J. E. G.

AMERICAN

CHEMICAL JOURNAL

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THE STRUCTURE OF THE SUBSTANCES OB-
TAINED BY THE ADDITION OF ORGANIC
OXYGEN COMPOUNDS AND ALUMIN-
IUM HALIDES.

By Elmer P. Kohler.

It is well known that the halogen compounds of alu-
minium combine with many organic compounds and that
the resulting addition-products play an important part in some
of the reactions in which aluminium compounds are used as
catalysts. Very little is known, however, about the proper-
ties of these products, and there is no experimental basis for
the structural formulas that have been proposed for them.
The object of the experiments described in this paper was to
ascertain whether the composition and properties of an impor-
tant class of these addition-products can be represented by
valence formulas and whether there is any relation between
these substances and salts with water of crystallization.

That aluminium halides combine with organic oxygen
compounds was discovered by Gustavson,[1] who found that
aluminium chloride combines with ethyl benzoate to form a

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[1] Ber. d. chem. Ges., **13**, 157.

substance whose composition is represented by the formula

$$AlCl_3.C_6H_5COOC_2H_5.$$
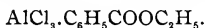
Shortly afterwards Combes[1] obtained a substance with the composition $AlCl_3.C_6H_7O_3$ as one of the products of the reaction between aluminium chloride and acetyl chloride, and Winogradoff,[2] working under Gustavson, obtained the substance $C_4H_4O_2Cl.AlCl_3$ as a second product of the same reaction. Later, Louise and Perrier[3] succeeded in isolating a crystalline substance with the composition

$$AlCl_3.C_6H_2(CH_3)_3COC_6H_5,$$
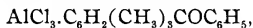
from the products of the reaction between aluminium chloride, mesitylene, and benzoyl chloride. This led Perrier[4] to undertake a systematic study of the reaction between aluminium chloride and organic oxygen compounds. Perrier found that aluminium chloride combines with acid chlorides, ketones, esters, phenols, borneol, and camphor. Of the addition-products obtained by Perrier, the most interesting are those with acid chlorides and ketones, since they represent successive stages in the synthesis of ketones by the Friedel and Crafts reaction. It is doubtful whether the compounds with phenols are formed by direct addition, as claimed by Perrier, since Claus and Mercklin[5] found that hydrochloric acid is evolved when aluminium chloride and phenols are brought together in an indifferent medium. To the product of the reaction between aluminium chloride and resorcinol they give the formula

$$C_6H_4\diagdown\!\!\!\!\!\diagup\substack{O\\O}\diagdown\!\!\!\!\!\diagup Al_2Cl_4$$
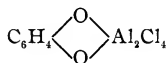
instead of the formula

$$C_6H_4(OH)_2.Al_2Cl_6$$
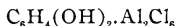
given by Perrier.

All the addition-products of organic oxygen compounds and aluminium chloride that have hitherto been analyzed, with the

[1] Ann. chim. phys., [6], **12**, 199.

[2] J. prakt. Chem., [2], **37**, 110.

[3] Compt. rend., **114**, 1377.

[4] *Ibid.*, **116**, 1140; **116**, 1298; **119**, 276.

[5] Ber. d. chem. Ges., **18**, 2934.

exception of the doubtful compounds with phenols, have the same general composition. They contain 1 molecule of an organic compound, which has at least one doubly-linked oxygen atom, in combination with 1 molecule of aluminium chloride. It is natural to assume, therefore, that this doubly-linked oxygen atom is in some way connected with the existence of the substances, and all the structural formulas that have been proposed for them are based on this assumption. For the substance prepared by Winogradoff, Gustavson[1] wrote the formula

$$CH_3COCH{=}C{<}^{Cl}_{O-AlCl_2},$$
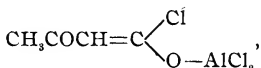
without offering any experimental evidence in its favor, and to the substance obtained by Combes he gave the formula

$$CH_3CO{\diagdown}_{CH_3CO}{\diagup}CH-C{-}^{Cl}_{Cl}{-}Cl_{O-AlCl_2},$$
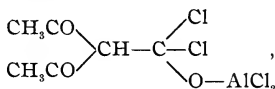
since he assumed that it was formed from the former by addition of acetyl chloride.

Kronberg[2] has recently proposed similar formulas for the addition-products of aluminium chloride and acid chlorides. For the compound with benzoyl chloride, for example, he suggests the formula

$$C_6H_5C{-}^{Cl}_{Cl}{-}Cl_{O-AlCl_2}.$$
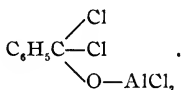
Kronberg uses this formula to account for the mechanism of the Friedel and Crafts reaction that was proposed, independently, by Perrier[3] and Boseken.[4]

The only evidence offered in favor of the formula is based on the analogy between benzotrichloride and the benzoyl chloride addition-product, as illustrated by the following equations:

[1] J. prakt. Chem. [2], **37**, 109.
[2] *Ibid.*, [2], **61**, 494.
[3] Compt. rend., **116**, 1300.
[4] Rec. trav chim. Pays-Bas, **19**, 19.

Kohler.

$$C_6H_5C\diagup^{Cl}_{\diagdown Cl} + C_6H_6 \quad = \quad C_6H_5C\diagup^{C_6H_5}_{\diagdown Cl} \quad + HCl;$$

$$C_6H_5C\diagup^{Cl}_{\diagdown OAlCl_2} + C_6H_6 \quad = \quad C_6H_5C\diagup^{C_6H_5}_{\diagdown OAlCl_2} \quad + HCl.$$
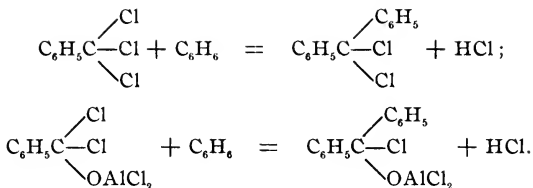
In a paper on the molecular weight of aluminium compounds[1] I showed that these addition-products have double the molecular weight that is usually assigned to them, and that the two halves of the molecules are linked together by the halogen atoms derived from aluminium chloride. This fact may be represented by writing the Gustavson-Kronberg formula,

$$C_6H_5C\diagup^{Cl}_{\diagdown O-Al-Cl} {}^{Cl = Cl}_{= Cl-Al-O} {}^{Cl}_{Cl-CC_6H_5}.$$
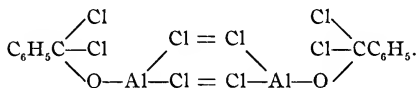
This formula can be tested by experiment. If it is correct, then only those oxygen compounds which have at least one doubly-linked oxygen atom can combine with aluminium chloride. The results described in this paper show that this is not the case, since ethers of all kinds combine with aluminium chloride and aluminium bromide. The products are crystalline substances whose composition and molecular weight are represented by the formula $(R_2O.AlX_3)_2$. They are, in every respect, exactly like the corresponding substances obtained from acid chlorides and ketones. The formulas of Gustavson and Kronberg are, therefore, wrong.

This leaves two possibilities : either these addition-products contain oxygen that has a higher valence than two, or else their formation does not depend upon the oxygen atoms in the organic substance. If the former is true, then the composition of the addition-products ought to vary with the number of oxygen atoms in a molecule of the organic compound. It is difficult to test this with aluminium chloride because of its insolubility in liquids that do not combine with it; but the

[1] This JOURNAL, **24**, 385.

results obtained with aluminium bromide are conclusive. It was found that the addition-products, with substances that have 1 atom of oxygen to the molecule, invariably contain 2 molecules of the oxygen compound to 1 "double" molecule of aluminium bromide, while the addition-products obtained from substances that have two atoms of oxygen generally contain only one molecule of the organic compound to one double molecule of aluminium bromide.

Terephthalyl chloride, for example, forms the compound $Al_2Br_6.C_6H_4(COCl)_2$, while the corresponding mono-acid chloride forms $Al_2Br_6.2C_6H_5COCl$. Similarly, diacetylmesitylene forms $Al_2Br_6.C_6H(CH_3)_3(COCH_3)_2$, while the corresponding mono-ketone combines with one-half as much of the bromide to form the compound $Al_2Br_6.2C_6H_2(CH_3)_3COCH_3$. These cases, and many similar ones, show that a substance that contains 2 atoms of oxygen to the molecule can combine with twice as much aluminium bromide as a substance that contains but one. The combination, therefore, probably takes place through oxygen.

All the facts that have been presented can be represented by the following formulas:

$$\text{I.} \quad \begin{array}{c} R \\ R \end{array}\!\!\!>\!\!O=ClAl(Cl_4)AlCl=O\!<\!\!\!\begin{array}{c} R \\ R \end{array} ;$$

$$\text{II.} \quad \begin{array}{c} R \\ R \end{array}\!\!\!>\!\!O\!<\!\!\!\begin{array}{c} Al(Cl_4)Al \\ Cl \end{array} \quad \begin{array}{c} \\ Cl \end{array}\!\!\!>\!\!O\!<\!\!\!\begin{array}{c} R \\ R \end{array}.$$
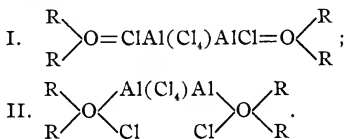
Formula I. is not in harmony with the behavior of many of the addition-products when they are heated. Acetylacetone, for example, combines with aluminium bromide to form a compound with the composition $Al_2Br_6.2C_5H_8O_2$. This decomposes at ordinary temperatures according to the equation

$$Al_2Br_6.2C_5H_8O_2 = Al_2Br_4.2C_5H_6O_2 + 2HBr.$$

The product of this decomposition combines with more acetylacetone, forming a new addition-product which also decomposes on heating, and the process of addition and decomposition can be repeated until the final product is pure

aluminium acetylacetone—a substance analogous to aluminium hydroxide. The addition-products with ethers and phenols behave in the same way. Thus, Hartmann and Gattermann[1] found that the substance, $Al_2Cl_6.2C_6H_5OCH_3$, decomposes at $120°$ according to the equation

$$Al_2Cl_6.2C_6H_5OCH_3 = Al_2Cl_4.2C_6H_5O + 2CH_3Cl,$$
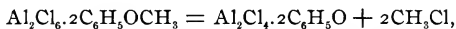
and Merz and Weith[2] found that when aluminium chloride is heated with phenol the final product is aluminium phenolate. All of these reactions are easily understood, if the structure of the addition-products is represented by formula II. The decomposition of the double compound with anisol, for example, takes place as follows :

$$\begin{array}{c}C_6H_5\\CH_3\end{array}\!\!>\!\!O\!\!<\!\!\begin{array}{c}Al(Cl_4)Al\\Cl\end{array}\!\!>\!\!O\!\!<\!\!\begin{array}{c}C_6H_5\\CH_3\end{array} = C_6H_5OAl(Cl_4)AlOC_6H_5$$
$$+ 2CH_3Cl.$$
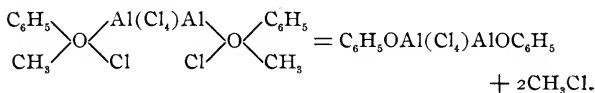
It is remarkable that 1 molecule of an aluminium halide never combines with more than 2 molecules of an organic oxygen compound while it combines with 6 molecules of an aromatic hydrocarbon.[3] Since many of the colored addition-products described in this paper change color when dissolved in benzene, it is probable that these substances also combine with aromatic hydrocarbons. After many attempts at isolating such addition-products I finally succeeded with anthraquinone, which forms the compound $Al_2Br_6.C_{14}H_8O_2.2C_6H_6$. This suggests, as a possible explanation of the Friedel and Crafts reaction, that the aluminium halide combines with both the acid chloride and the hydrocarbon, forming a complex molecule which subsequently undergoes a rearrangement similar to that observed in the case of the addition-product with acetylacetone. Such a mechanism would explain why the reaction takes place only with aromatic hydrocarbons.

It has been found, quite recently, that the composition and properties of a number of substances can be explained by the assumption that they contain quadrivalent oxygen. Since

[1] Ber. d. chem. Ges., **25**, 3531.
[2] *Ibid.*, **14**, 189.
[3] Gustavson : Jour. Russ. Phys. Chem. Soc., **10**, 305.

most of these substances have been obtained by the addition of acids to organic oxygen compounds, Baeyer and Villiger assume that quadrivalent oxygen has basic properties and that the substances are oxonium salts analogous to ammonium salts. There seems to be no difference between the addition of acids, described by Baeyer and Villiger, and that of salts described in this paper. The substances that combine with the former also combine with the latter, and the resulting addition-products resemble each other so closely that it is impossible to distinguish between them except by chemical methods. This is true, for example, in the case of dibenzalacetone. Baeyer and Villiger[1] conclude that the compound, $(C_6H_5CH=CH)_2CO.HCl$, cannot be a chlorhydrine because it is red, while the ketone chloride, $(C_6H_5CH=CH)_2CCl_2$, is colorless. Dibenzalacetone combines with aluminium halides as readily as it does with hydrochloric acid, and the resulting addition-products have the same brilliant red color that first drew attention to the compound with hydrochloric acid. The same relations hold in the case of a number of substances which dissolve in acids to form highly-colored solutions. Thus, the unsaturated ketones combine with aluminium bromide to form substances whose color is red ; xanthone, which is pale-yellow in color, and methylenephenylene ether, which is colorless, dissolve in concentrated sulphuric acid to form intensely yellow solutions and combine with aluminium halides to form compounds which have the same color as the acid solutions. There can be very little doubt that the addition-products of organic oxygen compounds with acids and those with salts like the aluminium halides have the same structure.

<div align="center">EXPERIMENTAL PART.</div>

<div align="center">*I. Compounds with Ethers.*</div>

The aluminium halides combine with aliphatic ethers with evolution of heat. The products are either liquids or very finely divided solids, which are almost impossible to wash and dry without serious decomposition. For this reason only the

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[1] Ber. d. chem. Ges., **34**, 2639.

crystalline compounds with aromatic ethers were purified and analyzed.

1. Phenyl Ether and Aluminium Bromide, $Al_2Br_6.2(C_6H_5)_2O$.
—Aluminium bromide dissolves in phenyl ether with evolution of heat, but it is difficult to isolate a pure substance from the solution. It is better to bring the substances together in carbon disulphide solution and precipitate the product with low-boiling petroleum ether. If the ether is carefully stratified on top of the solution the product crystallizes slowly in large lemon-yellow plates that are easily purified. The preparations used in the following experiments were washed with a mixture of petroleum ether and carbon disulphide and dried in a current of dry air.

To determine the amount of phenyl ether contained in the substance, a weighed quantity of the latter was decomposed with ice, the resulting liquid extracted with pure ether, the ethereal solution dried with a little fused calcium chloride, and evaporated in a weighing tube. The aluminium was determined as oxide by decomposing a weighed quantity with ice-water, evaporating the solution, and igniting the residue.

I. 1.6409 grams substance gave 0.6449 gram $(C_6H_5)_2O$.
II. 0.7265 gram substance gave 0.0850 gram Al_2O_3.

	Calculated for $Al_2Br_6.2(C_6H_5)_2O$.	Found.	
		I.	II.
$(C_6H_5)_2O$	38.91	39.30	....
Al	6.20	....	6.25

The substance is readily soluble in benzene and carbon disulphide, insoluble in ligroin. It is less stable than the corresponding addition-products with acids and ketones. When heated by itself it begins to decompose below 50°, and the following molecular weight determination shows that it is also partly dissociated in boiling carbon disulphide :

	Solvent. Grams.	Substance. Grams.	Elevation of boiling-point.	Molecular weight.
I.	37.35	1.3160	0.146	570.5
II.	"	2.7290	0.298	594.0
III.	"	4.3430	0.454	606.7
	Calculated for $Al_2Br_6.2(C_6H_5)_2O$,			874.16

The following determination made by the freezing-point method, using benzene as solvent, shows that the substance has the formula given to it :

	Substance. Grams.	Solvent. Grams.	Depression of freezing-point.	Molecular weight.
I.	20.45	0.9215	0.105	854.0
II.	"	2.0480	0.235	840.8
III.	"	2.9910	0.340	860.0

Mean, 851.6

Calculated for $Al_2Br_6.2(C_6H_5)_2O$, 874.16

2. Phenyl Ether and Aluminium Chloride, $Al_2Cl_6.2(C_6H_5)_2O$. —The substances were brought together in carbon disulphide and the product purified and analyzed like the corresponding compound with aluminium bromide.

The analysis gave the following results:

   I. 1.3661 grams substance gave 0.7708 gram $(C_6H_5)_2O$.
   II. 0.6421 gram substance gave 0.1085 gram Al_2O_3.
   III. 0.1622 gram substance gave 0.2370 gram AgCl.

	Calculated for $Al_2Cl_6.2(C_6H_5)_2O$.	I.	Found. II.	III.
$(C_6H_5)_2O$	56.18	56.43	....	....
Al	8.90	....	8.96	....
Cl	34.91	....	....	34.43

The substance crystallizes in pale-yellow plates, which are very readily soluble in benzene and carbon disulphide.

3. Anisol and Aluminium Bromide, $Al_2Br_6.2(C_6H_5OCH_3)$.—Equivalent quantities of anisol and aluminium chloride were brought together in carbon disulphide solution. The solution was cooled with ice-water and the product precipitated with petroleum ether. Unless the ether is added very slowly to the well-cooled liquid the product separates as an oil.

   I. 0.6866 gram substance gave 0.0961 gram Al_2O_3.
   II. 0.1841 gram substance gave 0.2745 gram AgBr.

	Calculated for $Al_2Br_6.2C_6H_5OCH_3$.	I.	Found. II.
Al	7.23	7.42	....
Br	63.96	....	63.68

The substance crystallizes in compact, pale-yellow prisms. It is very readily soluble in carbon disulphide, benzene, and anisol. The same product is obtained whether aluminium bromide or anisol is used in excess.

4. Anisol and Aluminium Chloride, $Al_2Cl_6.2C_6H_5OCH_3$.— Freshly distilled aluminium chloride was dissolved in an excess of anisol, the solution diluted with carbon disulphide, and the product precipitated with petroleum ether.

    I. 0.7217 gram substance gave 0.1573 gram Al_2O_3.

    II. 0.2002 gram substance gave 0.3614 gram AgCl.

	Calculated for $Al_2Cl_6.2C_6H_5OCH_3$.	I.	II.
Al	11.44	11.99	....
Cl	44.97	....	44.46

5. Methylenephenylene Ether and Aluminium Bromide, $Al_2Br_6.2C_{13}H_{10}O$.—A saturated solution of the ether in carbon disulphide was added, drop by drop, to a boiling solution of aluminium bromide in the same solvent. The product separated, on cooling, in the form of fine yellow needles. It was washed with a small quantity of cold carbon disulphide and recrystallized from a mixture of carbon disulphide and low-boiling petroleum ether.

    I. 0.8042 gram substance gave 0.3290 gram ether.

    II. 0.2654 gram substance gave 0.0293 gram Al_2O_3.

	Calculated for $Al_2Br_6.2C_{13}H_{10}O$.	I.	II.
$C_{13}H_{10}O$	40.54	40.91	....
Al	6.03	....	5.86

The substance is very soluble in carbon disulphide and benzene, almost insoluble in petroleum ether. At 90° to 100° it loses approximately 2 molecules of hydrobromic acid. The residue, on cooling, solidifies to a resinous mass, which could not be obtained in crystalline form. Water decomposes it into methylenephenylene ether and aluminium hydroxide.

II. Compounds with Ketones.

1. Acetophenone and Aluminium Bromide, $Al_2Br_6.2C_6H_5COCH_3$.—Equivalent quantities of the substances were brought together in carbon disulphide and the solution

evaporated in a current of dry air. The product was recrystallized from a mixture of benzene and petroleum ether and dried in a current of air.

I. 0.8204 gram substance gave 0.1099 gram Al_2O_3.
II. 0.2061 gram substance gave 0.4440 gram AgBr.

	Calculated for $Al_2Br_6.2C_6H_5COCH_3$.	I.	Found. II.
Al	7.00	7.12	....
Br	61.97	....	61.50

The substance crystallizes in small colorless plates, which are very slightly soluble in carbon disulphide, more readily in benzene.

2. *Acetylmesitylene and Aluminium Bromide,*

$Al_2Br_6.2C_6H_2(CH_3)_3COCH_3$.—A very dilute solution of acetylmesitylene in carbon disulphide was added to a solution of aluminium bromide in the same solvent and the liquid allowed to stand in a freezing-mixture. In the course of some hours the product separated in the form of large, pale-yellow plates. These were washed with carbon disulphide, dried, and analyzed.

I. 1.1240 grams substance gave 0.4225 gram ketone.
II. 0.8725 gram substance gave 0.1029 gram Al_2O_3.

	Calculated for $Al_2Br_6.2C_6H_2(CH_3)_3COCH_3$.	I.	Found. II.
$C_6H_2(CH_3)_3COCH_3$	37.79	37.59	....
Al	6.31	....	6.26

The substance is very slightly soluble in carbon disulphide and benzene, and has a tendency to separate from solution in the form of an oil which remains liquid for days unless brought in contact with a crystal of the same substance.

3. *Diacetylmesitylene and Aluminium Bromide,* $Al_2Br_6.$

$C_6H(CH_3)_3(COCH_3)_2$.—The addition-product separates out as a fine powder when a solution of diacetylmesitylene in carbon disulphide is added to a solution of aluminium bromide in the same solvent. The powder was repeatedly washed with boiling carbon disulphide and dried in a current of air.

I. 1.4321 grams substance gave 0.3766 gram ketone.
II. 0.8265 gram substance gave 0.1198 gram Al_2O_3.

	Calculated for $Al_2Br_6 \cdot C_6H(CH_3)_3(COCH_3)_2$.	Found. I.	II.
$C_6H(CH_3)_3(COCH_3)_2$	26.65	26.3	....
Al	7.45	....	7.67

The substance was obtained as a fine, reddish-yellow powder, but the color is probably due to some impurity, as the corresponding addition-product with dichloracetylmesitylene is almost colorless. The substance is insoluble in carbon disulphide, slightly soluble in boiling benzene. It dissolves fairly readily in a strong solution of diacetylmesitylene in carbon disulphide and crystallizes out unchanged on cooling. All efforts to get the substance corresponding to the addition-products with monoketones, $Al_2Br_6 \cdot 2C_6H(CH_3)_3(COCH_1)_2$, failed.

4. Chloracetylmesitylene and Aluminium Bromide, $Al_2Br_6 \cdot 2C_6H(CH_3)_3COCH_2Cl$. — Chloracetylmesitylene forms only one compound with aluminium bromide. The same substance was obtained in all of the following experiments: (*a*) equivalent quantities of the substances were brought together in carbon disulphide solution; (*b*) a solution of the ketone in carbon disulphide was gradually added to four times the calculated amount of the bromide dissolved in carbon disulphide; (*c*) a solution of the bromide was added to four times the calculated amount of the ketone dissolved in carbon disulphide; (*d*) a solution of the ketone in benzene was added to an excess of the bromide likewise dissolved in benzene; (*e*) the substances were brought together in nitrobenzene and the product precipitated with petroleum ether. The substance crystallizes well and is easily obtained in a pure condition.

I. 1.4114 grams substance gave 0.6012 gram ketone.

II. 0.7757 gram substance gave 0.0876 gram Al_2O_3.

	Calculated for $Al_2Br_6 \cdot 2C_6H_2(CH_3)_3COCH_2Cl$.	Found. I.	II.
$C_6H_2(CH_3)_3COCH_2Cl$	42.40	42.60	....
Al	5.85	....	5.95

5. Dichloracetylmesitylene and Aluminium Bromide, $Al_2Br_6 \cdot C_6H(CH_3)_3(COCH_2Cl)_2$. — A solution of the ketone in carbon disulphide was slowly added to a boiling solution of aluminium bromide in the same solvent. The precipitate was

washed with boiling carbon disulphide and dried in a current of air.

I. 0.9948 gram substance gave 0.3342 gram ketone.

II. 0.8264 gram substance gave 0.1033 gram Al_2O_3.

	Calculated for $Al_2Br_6.C_6H(CH_3)_3(COCH_2Cl)_2$	Found. I.	II.
$C_6H(CH_3)_3(COCH_2Cl)_2$	33.83	33.56	....
Al	6.72	....	6.63

The substance crystallizes in small, pale-yellow plates. It is sparingly soluble in boiling carbon disulphide and boiling benzene.

6. Dibenzalacetone and Aluminium Bromide,

$Al_2Br_6.2(C_6H_5CH : CH)_2CO$.—Equivalent quantities of dibenzalacetone and aluminium bromide were brought together in carbon disulphide solution. The addition-product separated immediately as a red crystalline precipitate.

I. 1.5420 grams substance gave 0.7247 gram ketone.

II. 0.7427 gram substance gave 0.0761 gram Al_2O_3.

	Calculated for $Al_2Br_6.2(C_6H_5CH : CH)_2CO$	Found. I.	II.
$(C_6H_5CH : CH)_2CO$	46.72	47.00	....
Al	5.41	....	5.56

The substance is only very slightly soluble in carbon disulphide. When prepared as described above, its color is exactly like that of the hydrochloric acid addition-product which is obtained on pouring fuming hydrochloric acid on dibenzalacetone. It dissolves slowly in boiling benzene and crystallizes out again, on cooling, in large, blood-red prisms. In the boiling solution the substance is probably almost completely dissociated, since at this temperature the solution is almost colorless. The color deepens as the temperature falls until, at the ordinary temperature, the color of the solution is the same as that of the addition-product which crystallizes out.

7. Anthraquinone and Aluminium Bromide, $Al_2Br_6.$

$C_6H_4 \underset{CO}{\overset{CO}{\diagdown\diagup}} C_6H_4$.—A solution of anthraquinone in boiling carbon disulphide was added, in small portions, to a boiling

solution of aluminium bromide in the same solvent. The product separated as a fine, brick-red, crystalline powder. This was washed with boiling carbon disulphide, dried, and analyzed.

I. 0.9895 gram substance gave 0.2754 gram anthraquinone.

II. 0.9962 gram substance gave 0.1385 gram Al_2O_3.

	Calculated for $Al_2Br_6.C_{14}H_8O_2$	Found. I.	II.
$C_{14}H_8O_2$	28.05	27.83	....
Al	7.30	....	7.35

The addition-product is insoluble in carbon disulphide. It dissolves slowly in boiling benzene to form a deep blood-red solution. A similar solution is obtained when aluminium bromide and anthraquinone are brought together in boiling benzene. On cooling the solution, a new substance crystallizes out in blood-red needles. The substance contains 2 molecules of benzene, which it slowly loses at ordinary temperatures, passing back into the brick-red powder described above. To determine the amount of benzene, the substance was heated to 50° in a current of dry air.

I. 1.4250 grams substance lost 0.2422 gram.

II. 1.8261 grams substance lost 0.3126 gram.

III. 1.5135 grams residue, after heating, gave 0.2118 gram Al_2O_3.

	Calculated for $Al_2Br_6.C_6H_4\!\!<\!\!{}^{CO}_{CO}\!\!>\!\!C_6H_4.2C_6H_6$.	Found. I.	II.	III.
C_6H_6	17.37	17.00	17.12	....
Al	7.30	....	....	7.76

The substance is extremely unstable. When poured into carbon disulphide or petroleum ether it immediately loses all its benzene, passing into the brick-red compound without going into solution.

8. Xanthone and Aluminium Bromide, $Al_2Br_6.2C_{13}H_8O_2$.— Equivalent quantities of xanthone and aluminium bromide were dissolved in boiling benzene. The product separated, on cooling, in long, yellow needles. After recrystallization from benzene, it was washed with cold carbon disulphide and dried in a current of air.

I. 0.9057 gram substance gave 0.3805 gram xanthone.

II. 0.2195 gram substance gave 0.0250 gram Al_2O_3.

	Calculated for $Al_2Br_6.2C_{13}H_8O_2$.	Found. I.	II.
$C_{13}H_8O_2$	42.33	43.00	....
Al	5.85	....	6.04

The substance is readily soluble in carbon disulphide and benzene.

9. Acetylacetone and Aluminium Bromide.—If a carbon bisulphide solution of aluminium bromide is added to a solution of acetylacetone in ligroin that is kept in a freezing-mixture, a colorless crystalline precipitate separates in fine needles. No hydrobromic acid is evolved during the reaction. It takes 1 molecule of aluminium bromide to precipitate 2 molecules of acetylacetone. If more than this is added the excess is found unchanged in the solution. The precipitate is, therefore, the addition-product $Al_2Br_6.2C_5H_8O_2$. The substance is so exceedingly unstable that it is impossible to dry it without loss of hydrobromic acid. If the temperature is allowed to rise the substance melts and gives off hydrobromic acid. The residue contains 2 atoms of bromine for every atom of aluminium. It is insoluble in carbon disulphide, but dissolves in a solution of acetylacetone containing 2 molecules of the latter for every molecule of aluminium bromide originally used. If this solution is evaporated, hydrobromic acid is given off and the residue contains 1 atom of bromine for 1 atom of aluminium. This residue also dissolves in a carbon disulphide solution of acetylacetone. If the solution is boiled, all the bromine is given off as hydrobromic acid, and pure aluminium acetylacetone crystallizes out when the solution is allowed to cool. Benzoylacetone behaves like acetylacetone, giving pure aluminium benzoylacetone. This is the best way to make aluminium derivatives of these diketones.

III. Compounds with Acid Chlorides.

1. Chloracetyl Chloride and Aluminium Bromide, Al_2Br_6. $2CH_2ClCOCl$.—Aluminium bromide dissolves in chloracetyl chloride. On cooling the solution, an addition-product sepa-

rates in pale-yellow plates. The same substance is formed when chloracetyl chloride is added to an excess of aluminium bromide dissolved in carbon disulphide. The substance was recrystallized from carbon disulphide. It is so exceedingly sensitive to moisture that it is almost impossible to dry it without loss.

I. 0.7227 gram substance gave 0.0990 gram Al_2O_3.

II. 0.1610 gram substance gave 0.2996 gram AgCl(Br).

| | Calculated for $Al_2Br_6.2CH_2ClCOCl.$ | Found. | |
		I.	II.
Al	7.13	7.26	....
Cl ⎫ Br ⎬	72.48	....	72.08

2. *Terephthalyl Chloride and Aluminium Bromide*, Al_2Br_6. $C_6H_4(COCl)_2$.—A solution of terephthalyl chloride in carbon disulphide was slowly added to an excess of aluminium bromide and the liquid boiled for an hour. The addition-product separated as a very finely divided pale-yellow powder. It was repeatedly washed with boiling carbon disulphide, dried, and analyzed.

I. 1.3252 gram substance gave 0.3021 gram terephthalic acid.

II. 0.6536 gram substance gave 0.0915 gram Al_2O_3.

III. 0.3414 gram substance gave 0.6486 gram AgCl(Br).

IV. 0.1821 gram substance gave 0.3480 gram AgCl(Br).

| | Calculated for $Al_2Br_6.C_6H_4(COCl)_2.$ | Found. | | | |
		I.	II.	III.	IV.
$C_8H_4O_4$	22.55	22.79	....	....	....
Al	7.45	....	7.77	....	....
Cl ⎫ Br ⎬	75.60	....	....	73.98	74.44

The substance is insoluble in carbon disulphide. It dissolves in a strong solution of terephthalyl chloride in carbon disulphide, but crystallizes out unchanged, as shown by the analysis (IV.) of a preparation obtained in this way.

3. *Terephthalyl Chloride and Aluminium Chloride*, Al_2Cl_6. $2C_6H_4(COCl)_2$.—Freshly prepared aluminium chloride was suspended in carbon disulphide and terephthalyl chloride added to the boiling liquid until all the aluminium chloride

dissolved. It took a little more than 2 molecules of tere-phthalyl chloride to dissolve 1 molecule of the salt. On cooling the solution the addition-product separated in large, transparent plates.

I. 1.2800 grams substance gave 0.6336 gram terephthalic acid.

II. 0.4950 gram substance gave 0.0762 gram Al_2O_3.

	Calculated for $Al_2Cl_6.2C_6H_4(COCl)_2$.	Found. I.	II.
$C_8H_4O_4$	49.90	49.60	....
Al	8.06	....	8.17

XCII.—ON THE ACTION OF PHENYLHYDRAZINE ON ACYLTHIOCARBAMIC AND ACYLIMIDO-THIOCARBONIC ESTERS: PYRRO-α,β'-DIAZOLE DERIVATIVES.

By HENRY L. WHEELER AND ALLING P. BEARDSLEY.

Acetoacetic ester and acetylurethane are attacked by phenylhydrazine in an analogous manner. In both cases the acetyl group, and not the carbethoxy group, is the point of attack by the amino (—NH_2) group of the hydrazine.

The ring-formed compounds that then result are derivatives of 1,3-dialkylpyrazole and 1,3-dialkylpyrrodiazole, respectively.

It might be expected that the thiourethanes—benzoylthiol, thion, and dithiocarbamates—would behave in a similar way. We have found, however, that the urethanes containing sulphur react with phenylhydrazine in precisely the opposite manner; that the —NH_2 group of the hydrazine reacts with the ester group and not with the benzoyl group. Hydrogen sulphide or mercaptan is evolved and 1,5-dialkylpyrrodiazole (triazole) derivatives result instead of the isomeric 1,3 compounds. Examples of the reactions of four types of acylurethanes are tabulated below. They illustrate more definitely the above statements, and they show that four different series of pyrro-α,β'-diazole derivatives result in the reactions in ques-

17-27

tion. The products in I., II., and IV. may naturally be represented as having the tautomeric CO and CS structures :

$$\text{I.} \quad \begin{array}{c} CH_3CONHCO.OC_2H_5 \\ + \\ H_2N-NHC_6H_5 \end{array} = \begin{array}{c} CH_3C-N=COH \\ \| \quad\quad | \\ N\text{——}NC_6H_5 \end{array} + \begin{array}{c} H_2O \\ \\ C_2H_5OH \end{array} ;$$

$$\text{II.} \quad \begin{array}{c} C_6H_5CONHCO.SC_2H_5 \\ + \\ C_6H_5NH-NH_2 \end{array} = \begin{array}{c} C_6H_5C=N-COH \\ | \quad\quad | \\ C_6H_5N\text{——}N \end{array} + \begin{array}{c} C_2H_5SH \\ \\ H_2O \end{array} ;$$

$$\text{III.} \quad \begin{array}{c} C_6H_5CONHCS.OC_2H_5 \\ + \\ C_6H_5NH-NH_2 \end{array} = \begin{array}{c} C_6H_5C=N-COC_2H_5 \\ | \quad\quad \| \\ C_6H_5N\text{——}N \end{array} + \begin{array}{c} H_2S \\ \\ H_2O \end{array} ;$$

$$\text{IV.} \quad \begin{array}{c} C_6H_5CONHCS.SC_2H_5 \\ + \\ C_6H_5NH-NH_2 \end{array} = \begin{array}{c} C_6H_5C=N-CSH \\ | \quad\quad \| \\ C_6H_5N\text{——}N \end{array} + \begin{array}{c} C_2H_5SH \\ \\ H_2O \end{array} .$$

The product in reaction I. was first obtained as above by Andreocci,[1] and the above constitution, *i. e.*, 1-phenyl-3-methyl-5-oxytriazole, was assigned to the compound. This was proved to be correct by Bamberger and de Gruyter,[2] and by Widman.[3]

The product obtained by us in reaction II. proved to be identical, in every respect, with the oxytriazole prepared by Young[4] from phenylsemicarbazide, benzaldehyde, and ferric chloride ; and by Widman[5] by warming benzoylphenylsemicarbazide with alkali.

The reaction represented by equation III. was investigated by Wheeler and Johnson,[6] in the case of methyl benzoylthioncarbamate, and the product was shown to be 1,5-diphenyl-3-methoxytriazole, by boiling with hydrochloric acid, whereupon the triazole of Young and Widman was obtained.

The proof that the mercaptotriazole formed in reaction IV. is 1,5-diphenyl-3-mercaptotriazole follows from the fact that the same compound results by warming alcoholic solutions of phenylthiosemicarbazide, benzaldehyde, and ferric chloride. This product is entirely different from the isomeric 1,3-di-

1 Ber. d. chem. Ges., **22**, R. 737 (1889).
2 *Ibid.*, **26**, 2385.
3 *Ibid.*, **26**, 2617 (1893).
4 J. Chem. Soc., **67**, 1063 (1895).
5 Ber. d. chem. Ges., **29**, 1951 (1896).
6 This JOURNAL, **24**, 198 (1900).

phenyl-5-mercaptotriazole, which we have prepared from benzoyl rhodanide, formylphenylhydrazine, and alkali. This procedure affords a new method for the preparation of triazole derivatives, and the reaction takes place as follows:

$$
\begin{array}{c}
C_6H_5CONCS \\
+ \\
HCONH-NHC_6H_5
\end{array}
=
\begin{array}{c}
C_6H_5C-N=C-SH \\
\| \quad\quad | \\
N----NC_6H_5
\end{array}
+ \; HCOOH.
$$
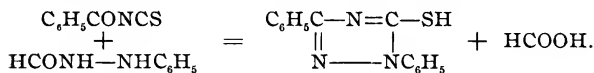
In this reaction another compound is formed that is insoluble in alkali. This material agrees in composition with 1,3-diphenyl-2-formyl-5-thiotriazole or 1-phenyl-4-benzoyl-5-thiotriazole or α'-benzoylimido-β'-phenylthiobiazoline. At present, the evidence is in favor of its being regarded as the last-mentioned compound, since on boiling with alkali it decomposes and is not converted into a triazole.

The two products, formed by the action of phenylhydrazine on the benzoyldithiocarbamates on the one hand, and from phenylthiosemicarbazide, benzaldehyde, and ferric chloride on the other, were conclusively shown to be the same by the identity of their alkyl derivatives. These latter, in turn, were identical with the compounds formed by treating the benzoylimidodithiocarbonic esters with phenylhydrazine. Phenylhydrazine therefore acts on the latter series of compounds as follows:

$$
\text{V.} \quad
\begin{array}{c}
C_6H_5CON=C{<}^{SCH_3}_{SCH_3} \\
+ \\
C_6H_5NH-NH_2
\end{array}
=
\begin{array}{c}
C_6H_5C=N-CSCH_3 \\
| \quad\quad \| \\
C_6H_5N----N
\end{array}
+
\begin{array}{c}
CH_3SH \\
H_2O
\end{array}.
$$
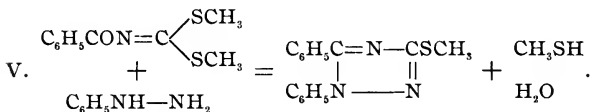
In the case of the above classes of compounds, the tendency of the groups to react with hydrogen of the amino group in phenylhydrazine may be expressed by the following arrangement:

$$
CSAlk > CS > CO > COAlk.
$$
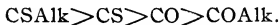
That is to say, mercaptan is eliminated, rather than hydrogen sulphide, and both these products more readily than water or alcohol, the latter having the least tendency to separate. From this it might be predicted that the acylimidomonothiocarbonic esters would react as follows:

$$\text{VI.} \quad \begin{array}{c} C_6H_5CON=C{\Large\langle}\genfrac{}{}{0pt}{}{OC_2H_5}{SC_2H_5} \\ + \\ C_6H_5NH-NH_2 \end{array} = \begin{array}{c} C_6H_5C=N-COC_2H_5 \\ | \quad\quad || \\ C_6H_5N-\!\!-\!\!-N \end{array} + \begin{array}{c} C_2H_5SH \\ \\ H_2O \end{array} .$$
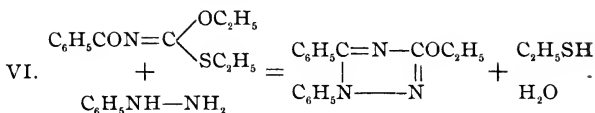
We have found that the reaction takes place as indicated, that mercaptan and water are liberated, and that 1,5-diphenyl-3-ethoxytriazole is formed. In this case it was easy to show that the reaction takes place in two stages. When phenylhydrazine was mixed with benzoylimidothioethyl carbonate in benzene, mercaptan alone was evolved, and the product obtained was benzoylpseudoethylphenylsemicarbazide,

$$C_6H_5CO-NH-C(OC_2H_5)=N-NHC_6H_5.$$

This intermediate product can be crystallized from alcohol and is stable below 136°, at which temperature it loses water and is smoothly converted into 1,5-diphenyl-3-ethoxytriazole.

The stability of this product is especially significant, as it affords an indication of the mechanism of the above reactions. If the acylurethanes are represented as having the pseudo form, $CH_3C(OH)=NCOOC_2H_5$ or $C_6H_5CON=C(OH)SC_2H_5$, etc., then these, as well as the acylimidocarbonic esters, contain a 1,4 double union, $O=\overset{|}{C}-N=C<$; and phenylhydrazine might be expected to add[1] to these compounds, according to Thiele's theory, in the 1,4 position, as represented by formula VII. This sort of reaction would appear to satisfactorily explain the above triazole formations, were it not for the fact that in the present case it is difficult to reconcile the stability of the intermediate product with this formula.

$$\begin{array}{c} C_6H_5C(OH)=N-C{\Large\langle}\genfrac{}{}{0pt}{}{OC_2H_5}{SC_2H_5} \\ | \quad\quad\quad\quad\quad H \\ C_6H_5NH-\!\!-\!\!-N \end{array} \qquad \begin{array}{c} C_6H_5CO-NH-C{\Large\langle}\genfrac{}{}{0pt}{}{OC_2H_5}{SC_2H_5} \\ | \quad\quad\quad\quad\quad H \\ C_6H_5NH-\!\!-\!\!-N \end{array}$$

$$\text{VII.} \qquad\qquad\qquad\qquad\qquad \text{VIII.}$$
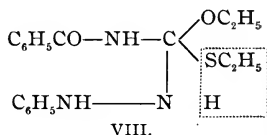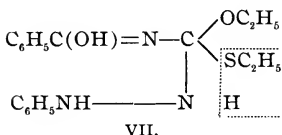
A compound with an enol structure, such as VII., would separate water and form the triazole more readily than the

[1] That the action of amines on the acylthioncarbamic esters takes place by addition has already been shown in a previous paper. This JOURNAL, **24**, 189 (1900).

keto form, VIII., and, therefore, the latter better represents the course of the reaction.

The fact observed by Widman[1] that benzoylphenylsemicarbazide, $C_6H_5CON(C_6H_5)NHCONH_2$, is not transformed into a triazole by heating with acid chlorides, acid anhydrides, or by strongly heating alone, is probably to be explained by the absence of hydrogen adjacent to the benzoyl group. When, however, this compound is treated with alkali it readily gives 1,5-diphenyl-3-oxytriazole. In other words, it appears to us that an unstable alkali addition-product is formed, as has frequently been observed in the case of acid amides, namely,

$$C_6H_5CO(OH.ONa)—NC_6H_5—NHCONH_2,$$
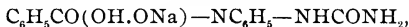
and as this affords the necessary enol condition, the material then readily undergoes condensation.

Now, with this explanation, we were confronted with what at first appeared to be a serious difficulty in accounting for the ease with which the acylthiocarbamates directly form triazoles. For, if the action of phenylhydrazine on benzoyldithiocarbamates, $C_6H_5CONHCS.SR$, results in the formation of a compound analogous to VIII., then by separation of mercaptan, benzoylphenylthiosemicarbazide, $C_6H_5CONH—CS—NH—NHC_6H_5$,[2] must be the intermediate product.

A compound that is represented as having this structure has been prepared by Dixon[3] by combining phenylhydrazine with benzoyl rhodanide. This, however, does not melt even at 220°, while the mercaptotriazole melts at 187° and is easily formed at the temperature of the steam-bath.

In our first experiments we heated the benzoylthiocarbamates with a slight excess of phenylhydrazine, and under these conditions no intermediate product was observed. This suggested the thought that the slight excess of phenylhydrazine employed might have acted by catalysis on the intermediate products, like alkali in the above case. The enol condition thus produced would then readily give rise to condensation. Acting on this supposition, we thereupon carried out the reaction with benzoyldithioethylcarbamate in a cold, dilute, al-

[1] *Loc. cit.* See also Young and Annable : J. Chem. Soc., **71**, 204 (1897).

[2] Or a tautomeric form.

[3] J. Chem. Soc. **55**, 304 (1889).

coholic solution; mercaptan almost immediately made its presence known, and after standing some time a beautifully crystallized mass of material separated, which proved to be the desired intermediate product.

The curious fact was then observed that this compound melted at 136° and was, therefore, different from the expected benzoylphenylthiosemicarbazide of Dixon. When our material was heated above its melting-point, it gave off water and passed smoothly into 1,5-diphenyl-3-mercaptotriazole, a reaction showing the substance to have the structure which Dixon has assigned to his compound. The explanation of the structure of the latter compound, which now does not immediately concern us, will receive attention at a later time.[1]

The catalytic effect of phenylhydrazine on our benzoylphenylthiosemicarbazide, at the temperature of boiling alcohol, proved to be precisely what was expected. The substance can be repeatedly crystallized from alcohol without alteration. If a couple of drops of phenylhydrazine are added, however, and the boiling continued, the material is quantitatively converted into the mercaptotriazole. The same transformation takes place in the cold with alkali.

The above experiments conclusively show that in these 1,4 unsaturated compounds, a 1,2 and not a 1,4 addition or attack takes place. This is in all probability due to the fact that the form —CONH— is more stable than —COH=N— and that hydrogen has a greater tendency to attach itself to nitrogen than to oxygen.[2]

<div align="center">EXPERIMENTAL PART.</div>

Methyl Benzoylthiolcarbamate, $C_6H_5CONHCOSCH_3$, *and Phenylhydrazine.*—Molecular quantities of the carbamate and phenylhydrazine were mixed in a little alcohol and warmed for several hours on the steam-bath. After the evolution of mercaptan had ceased, the alcohol was evaporated and the residue was treated with warm dilute alkali, whereupon, on

[1] Since the above was written Dr. T. B. Johnson has examined this product and found that it is 1,3-diphenyl-5-mercaptotriazole. See experimental part of this paper.

[2] For other exceptions see Thiele : Ann. Chem. (Liebig), **306**, 105 (1899) ; **319**, 129 (1901).

acidifying and boiling the precipitate with alcohol, 1,5-diphenyl-3-oxytriazole, melting at 290°, was obtained. A comparison of this material with the product obtained by Young's method[1] showed that the two samples were identical, and when mixed the melting-point was not lowered.

Benzyl Benzoyldithiocarbamate, $C_6H_5CONHCS.SCH_2C_6H_5$, *and Phenylhydrazine.*—The carbamate (30.5 grams) and phenylhydrazine (11.3 grams) were mixed without a solvent, whereupon heat was evolved, and after warming about three hours on the steam-bath the action was complete. The material then crystallized from alcohol in bunches of fine, colorless needles, melting at 187° to 187°.5.

This compound was also obtained from benzoyldithiocarbamic ethylacetate, $C_6H_5CONHCS.SCH_2CO_2C_2H_5$ (5 grams), and phenylhydrazine (1.9 grams). Only a trace of blackening of silver nitrate paper was observed in this preparation (yield of purified material 3.5 grams). Nitrogen determinations gave :

	Calculated for $C_{14}H_{11}N_3S$.	Found. I.	Found. II.
N	16.60	16.38	16.22

It was shown that this product is 1,5-diphenyl-3-mercaptotriazole by preparing it from phenylthiosemicarbazide, benzaldehyde, and ferric chloride. The yield is poor (40 grams of phenylthiosemicarbazide gave about 2.8 grams of the triazole). Prepared in this way it is difficult to purify, and, after repeated crystallizations from alcohol it melted from 0°.5 to 1° too low. When it was mixed with the above material its melting-point was not lowered. The identity of the two products was conclusively shown by the preparation of the ethyl acetate derivatives (see below).

1,5-Diphenyl-3-mercaptotriazole is difficultly soluble in cold alcohol, more readily in hot and in benzene. It is readily soluble in aqueous alkali, and it can be boiled with strong potassium hydroxide with little effect. Its sodium salt is readily soluble in alcohol. In fact, this triazole and its derivatives are characterized by their great stability. It cannot be desulphurized by boiling with freshly precipitated mercuric

[1] *Loc cit.*

oxide. From its solution in ammonia silver nitrate precipi-
tates a bulky, white, amorphous silver salt which is not de-
composed by boiling.

An attempt was made to prepare the mercaptotriazole from
1,5-diphenyl-3-chlortriazole,[1] but it was found that this chlo-
ride could be fused with potassium hydrosulphide and recov-
ered unaltered.

Ethyl Benzoyldithiocarbamate, $C_6H_5CONHCSSC_2H_5$, *and
Phenylhydrazine.*—Seven grams of the former and 3.3 of the
latter were mixed in 25 cc. of alcohol and allowed to stand for
several hours. Mercaptan made its presence known almost at
once, and finally a mass of colorless, six-sided plates or tables
separated that had every appearance of being pure. This ma-
terial melted at 136°–137°, showing signs of melting at 134°,
and three crystallizations from alcohol failed to alter the melt-
ing-point. On rapidly cooling the alcoholic solutions, the ma-
terial crystallized in long, slender prisms, which to the naked
eye appeared as needles. A nitrogen determination agreed
with the calculated for benzoylphenylthiosemicarbazide,
$C_6H_5CONHCSNH-NHC_6H_5$:

	Calculated for $C_{14}H_{13}ON_3S$.	Found.
N	15.49	15.65

When this substance was heated above its melting-point it
effervesced vigorously at 170° to 180°. On crystallizing then
from alcohol it melted at 187° and was found to have been
transformed into 1,5-diphenyl-3-mercaptotriazole.

One gram of the material was dissolved in alcohol and 2 or
3 drops of phenylhydrazine were added; on evaporating to
dryness and crystallizing from alcohol, in which the material
was then much less readily soluble, it was found that the sub-
stance had been converted into the above triazole.

A portion was dissolved in cold dilute sodium hydroxide and
immediately precipitated by dilute hydrochloric acid, where-
upon, without further purification, it melted at 187° to 187°.5.

1,5-Diphenyltriazole-3-monosulphide, $(C_{14}H_{10}N_3)_2S$.—Three
grams of the mercaptotriazole and 20 grams of aniline were
heated in a closed tube at 270° to 300° for twelve hours. On

[1] Cleve : Ber. d. chem. Ges., **29,** 2672 (1896).

cooling only slight pressure was found in the tube, due to hydrogen sulphide. The contents of the tube were dissolved in alcohol and precipitated with dilute sodium hydroxide. The insoluble part was crystallized from alcohol, whereupon bulky needles of a pinkish-brown shade were obtained which melted at 198°.

This compound was also obtained by heating the mercaptotriazole with paratoluidine at about 180° for thirty hours.

Sulphur determinations gave :

	Calculated for $C_{28}H_{20}N_6S$.	Found.	
		I.	II.
S	6.77	6.96	7.29

1,5-Diphenyltriazole-3-disulphide, $(C_{14}H_{10}N_3)_2S_2$.—The mercaptotriazole was dissolved with one molecular proportion of sodium ethylate in alcohol and somewhat over the calculated quantity of iodine was added. The alcohol was then evaporated and the residue was crystallized from alcohol, whereupon small, colorless pyramids or sharp-pointed crystals, like arrow-heads, were obtained, which melted at 174°. The material was free from iodine, and a nitrogen determination gave :

| | Calculated for $C_{28}H_{20}N_6S_2$. | Found. |
| N | 16.66 | 16.46 |

1,5-Diphenyl-3-benzoylmercaptotriazole.—Molecular proportions of mercaptotriazole, sodium ethylate, and benzoyl chloride were mixed in alcoholic solution ; the alcohol was then evaporated, the residue washed with water, and crystallized from alcohol, whereupon beautiful, colorless needles, melting at 138°.5, were obtained. A nitrogen determination gave :

| | Calculated for $C_{21}H_{15}ON_3S$. | Found. |
| N | 11.78 | 12.03 |

1,5-Diphenyl-3-methylmercaptotriazole was prepared from benzoylimidodithiomethyl carbonate and phenylhydrazine (by Dr. T. B. Johnson) and also by methylating the mercaptotriazole by means of sodium ethylate and methyl iodide. In both cases beautiful, colorless tables or six-sided plates, melting at 102° to 103°, were obtained on crystallizing from alcohol.

A nitrogen determination was made from a specimen obtained by the first method.

	Calculated for $C_{15}H_{13}N_3S$.	Found.
N	15.73	15.79

Strong aqueous potash has no effect on this compound. When fused with potassium hydroxide it dissolves, and on acidifying, the mercaptotriazole melting at 187° is obtained.

1,5-Diphenyl-3-ethylmercaptotriazole was obtained by ethylating the mercaptotriazole by means of sodium ethylate and ethyl bromide. On crystallizing from alcohol it forms long, slender, colorless prisms melting at 97°. A nitrogen determination gave:

	Calculated for $C_{16}H_{15}N_3S$.	Found.
N	14.9	15.2

1,5-Diphenyl-3-ethylacetatemercaptotriazole was obtained from the mercaptotriazole prepared from phenylthiosemicarbazide, as well as from that prepared by means of benzyl benzoyldithiocarbamate and phenylhydrazine. In both cases beautiful, colorless prisms were obtained which melted at 67°. When the samples were mixed the melting-point was not lowered. A nitrogen determination gave:

	Calculated for $C_{18}H_{17}O_2N_3S$.	Found.
N	12.39	12.52

1,5-Diphenyl-3-benzylmercaptotriazole.—This was obtained in three ways. It was first prepared by warming molecular quantities of benzoylimidodithiobenzylcarbonic ester and phenylhydrazine on the steam-bath. The mercaptan evolved was removed by distilling under diminished pressure and the residue was crystallized from alcohol, whereupon beautiful, flattened, colorless prisms, clustered in the form of balls, were obtained. These melted at 100° to 100°.5, and a nitrogen determination was made with the result given below.

This compound was also obtained by treating the mercaptotriazole with alkali and benzyl chloride.

	Calculated for $C_{21}H_{17}N_3S$.	Found.
N	12.24	12.27

It was found that this compound was the chief product when phenylhydrazine was allowed to act on the following ester :

Di(benzoylimidodithiobenzyl)ethylene Ester, $C_6H_5CON=C(SCH_2C_6H_5)SCH_2CH_2S(C_6H_5CH_2S)C=NCOC_6H_5$. —– This was prepared from benzoyldithiobenzyl carbamate by means of sodium ethylate and ethylene bromide in alcoholic solution. It crystallizes from alcohol in the form of fine, colorless, radiating needles, having a faint green tinge, and it melts at 93°.5 to 94°. A nitrogen determination gave :

	Calculated for $C_{32}H_{28}O_2N_2S_4$.	Found.
N	4.66	4.84

The Ethylacetate Derivative of Acetyldithiocarbamic Acid, $CH_3CONHCSSCH_2CO_2C_2H_5$.—This was made by warming thiocyanethylacetate with thioacetic acid. It formed yellow needles or slender prisms from a mixture of benzene and petroleum ether, which melted at 82°, and a nitrogen determination gave :

	Calculated for $C_7H_{11}O_3NS_2$.	Found.
N	6.33	6.51

When 2.7 grams of this were mixed with 1.5 grams of phenylhydrazine, in some alcohol, and warmed for several hours on the steam-bath, a product was obtained which crystallized from alcohol in colorless prisms and was difficultly soluble. It melted at 163° to 164° and a nitrogen determination agreed with the calculated for *1-phenyl-5-methyl-3-mercaptothiazole* :

	Calculated for $C_9H_9N_3S$.	Found.
N	21.9	21.7

1-Paratolyl-5-phenyl-3-mercaptotriazole, from normal propyl-benzoyldithiocarbamate and paratolylhydrazine, formed colorless needles or prisms, from alcohol, which melted at 170° to 171°, showing signs of melting at 168°. A nitrogen determination gave :

	Calculated for $C_{15}H_{13}N_3S$.	Found.
N	15.73	16.00

Benzoylimidomonothioethylcarbonate, $C_6H_5CON=C{<}{\overset{OC_2H_5}{SC_2H_5}}$,
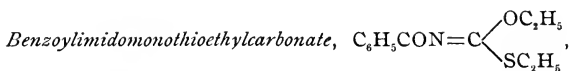
and Phenylhydrazine.—When molecular quantities of the
above substances were dissolved in benzene the odor of mer-
captan was soon noticed, and on standing several hours a mass
of crystals separated. On crystallizing these from alcohol,
radiating groups of fine needles were obtained which melted
at 136°, with effervescence due to the escape of water. A ni-
trogen determination agreed with the calculated for benzoyl-
pseudoethylphenylsemicarbazide, $C_6H_5CONHC(OC_2H_5)=$
$N{-}NHC_6H_5$:

	Calculated for $C_{16}H_{17}O_2N_3$.	Found.
N	14.8	15.1

When the calculated quantities of the above carbonate and
phenylhydrazine were mixed and heated in a bath at 140°,
mercaptan and water were evolved, and on crystallizing the
residue from dilute alcohol, fine needles were obtained which
melted at 90°. Young[1] gives the melting-point of 1,5-di-
phenyl-3-ethoxytriazole as 92°. We therefore prepared this
substance by his method and found that it also melts at 90°,
and that on mixing the two products no reduction in
melting-point took place.

One gram of the pseudosemicarbazide was dissolved in alco-
hol and 3 drops of phenylhydrazine were added. The mix-
ture was evaporated on the steam-bath, and, after about an
hour, crystallized from alcohol, whereupon it was found that
the material had been converted into the ethoxytriazole
which melts at 90°.

1,3-Diphenyl-5-mercaptotriazole.—This mercaptotriazole, iso-
meric with the one obtained from the benzoyldithiocarbamates
and phenylhydrazine, was prepared as follows: Five grams
of formylphenylhydrazine and 6 of benzoylrhodanide were
mixed and heated sufficiently to melt the mixture. The ma-
terial was then allowed to remain on the steam-bath for a
number of hours. It was then treated with cold dilute sodium
hydroxide, filtered from insoluble material, and the triazole

[1] *Loc. cit.*

precipitated by dilute hydrochloric acid. The precipitate, on crystallizing from alcohol, formed pure white, hair-like bunches of needles, which sinter and then melt at about 248° to 249°. The following results were obtained on analysis:

	Calculated for $C_{14}H_{11}N_3S$.	Found.
N	16.60	16.38
S	12.65	12.85

The material insoluble in alkali was crystallized from alcohol, whereupon long needles or thin prisms were obtained which melted at 119° to 120°. This formed the larger part of the above reaction-product. The analytical results agreed with the calculated for a condensation of equal molecules of benzoyl rhodanide and formylphenylhydrazine minus water.

	Calculated for $C_{16}H_{11}ON_3S$.	Found.
N	14.9	15.1
S	11.39	10.79

A portion of the material was boiled with dilute alkali; nearly all dissolved and an odor of aniline or phenylhydrazine was noticed. On adding dilute hydrochloric acid, benzoic acid was precipitated. Benzoic acid was also obtained on warming with dilute hydrochloric acid. These experiments show that the material is easily decomposed. From this it is improbable that the compound is a triazole, and, therefore, at present we are inclined to the view that it is $α'$-benzoylimido-$β'$-phenylthiobiazoline,

$$\begin{array}{c} C_6H_5N\text{———}N \\ | \qquad \| \\ C_6H_5CON=C\text{—}S\text{—}CH \end{array}.$$
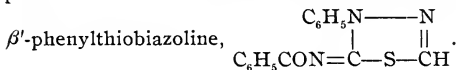
αα-Carbethoxyphenylsemicarbazide,

$C_2H_5OCO(C_6H_5)N$—$NHCONH_2$, was prepared from phenyl-semicarbazide and an excess of chlorcarbonic ester by warming on the water-bath. It was crystallized from a mixture of alcohol and benzene (2 volumes of alcohol and 3 volumes of benzene). Rapid crystallization produced bunches of very fine, hair-like needles, while slow gave compact bunches of small prisms. It melts at 171.5°, and a nitrogen determination gave:

	Calculated for $C_{10}H_{13}O_3N_3$.	Found.
N	18.83	18.78

This substance is difficultly soluble in benzene, quite soluble in alcohol, and it may be crystallized from water. With sodium hydroxide, sodium ethylate, and acetyl chloride, phenylurazole melting at 263° is formed. Boiling chlorcarbonic ester has no effect on the compound, while if it is melted it decomposes. When warmed with phenylhydrazine, on the water-bath, it remained unaltered.[1]

NEW HAVEN, CONN., Feb. 6, 1902.

XCIII.—ON THE MOLECULAR REARRANGEMENT OF UNSYMMETRICAL ACYLTHIOUREAS AND ACYLPSEUDOTHIOUREAS TO ISOMERIC SYMMETRICAL DERIVATIVES.

BY HENRY L. WHEELER.

The interesting observation was made by Hugershoff[2] that by the action of acetic anhydride on monophenylthiourea an unstable acetylphenylthiourea first results, which melts at 139°. On heating this substance above its melting-point a molecular rearrangement takes place, and the material is transformed into an isomeric acetylphenylthiourea melting at 171°. The latter is identical with the product obtained from acetylisothiocyanate and aniline.[3] These isomers are sharply distinguished by their properties, and especially by their behavior with mercuric oxide and with alkali. Hugershoff found that the labile acetyl derivative, melting at 139°, is readily desulphurized by mercuric oxide, yielding acetylphenylurea, while the stable derivative, obtained by heating

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[1] In the February number of this JOURNAL, Acree describes this compound as dicarbethoxyphenylsemicarbazide and two carbon and hydrogen determinations are given in support of his view. The amount of carbon for a mono- and dicarbethoxy derivative differs by only 0.98 per cent., while that of hydrogen is the same. On the other hand, that of nitrogen differs by 4.60 per cent. We, therefore, prepared the compound by Acree's directions and observed that the material melted at 171.5° and when mixed with ours the melting-point was not altered. A nitrogen determination gave:

	Calculated for $C_{12}H_{17}O_5N_3$.	Calculated for $C_{10}H_{13}O_3N_3$.	Found.
N	14.23	18.83	19.20

The compound is therefore a monocarbethoxy derivative. Acree states that on crystallizing his material from water the melting-point is lowered. Our material was found to behave in the same manner.

[2] Ber. d. chem. Ges., **32**, 3649 (1899).

[3] Miquel: Bull. Soc. Chim., [1], **25**, 252.

the labile one, is unaffected by mercuric oxide. He concludes, from the analogous behavior of diphenylthiourea, that this action of mercuric oxide alone is sufficient to show that the labile acetyl derivative has the following structure:

$$C_6H_5NHCSNHCOCH_3.$$
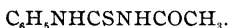
For the stable derivative the isomeric pseudo or tautomeric form, $C_6H_5N=C(SH)NHCOCH_3$, is assumed. The existence of these isomers is, according to this, merely a case of desmotropism.

Both the labile and stable derivatives dissolve in alkali of a dilution of 15 : 1000. On subsequently precipitating with carbon dioxide or hydrochloric acid, only the stable form is obtained. With strong alkali, 15 : 100, the labile does not dissolve, but a mass of crystals of acetanilide and phenylthiourea almost immediately form, while in solution are the sodium salts of thiocyanic and acetic acids. The stable urea, on the other hand, dissolves in strong alkali and can be reprecipitated unaltered.

Besides monophenylthiourea, several other monoarylthioureas were found to give isomeric acetyl derivatives,[1] but disubstituted ureas, diphenylthiourea, etc., gave only one acetyl compound.

In regard to other explanations of the existence of these isomers, the possibility that they are stereochemical modifications was considered, only to be rejected on account of the behavior of the labile ureas toward mercuric oxide.

The idea that the labile acetyl derivatives are unsymmetrical acetylarylureas, $CH_3CO(C_6H_5)N—CS—NH_2$, is not mentioned by Hugershoff, although the lack of corresponding isomers in the case of disubstituted ureas is especially significant, and moreover, the behavior of the labile compounds with strong alkali will scarcely permit of any other explanation.

The writer proposes to show now that these labile ureas belong to the hitherto unknown or unrecognized class of unsymmetrical acylthioureas, and that the isomerism in question does not depend on the existence of both a normal and a pseudo form. This is proved as follows : In a previous paper

[1] Hugershoff and König : Ber. d. chem. Ges., **33**, 3029 (1900).

it was shown by Wheeler and Johnson[1] that dimethyl acetyl-imidodithiocarbonate reacts with aniline, giving symmetrical acetylphenylpseudomethylthiourea (I). The position of the acetyl group in the resulting acylpseudourea is shown by its method of formation :

$$CH_3CON=C \begin{array}{l} SCH_3 \\ SCH_3 \end{array} + H_2NC_6H_5 =$$

$$CH_3CON=C \begin{array}{l} NHC_6H_5 \\ SCH_3 \end{array} + CH_3SH.$$

I.
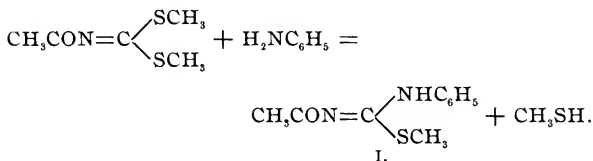
Now by careful treatment of phenylpseudomethylthiourea, $H_2N-C(SCH_3)=NC_6H_5$, with acetyl chloride a product can be obtained isomeric with the above acetylphenylpseudomethylthiourea. Since only two structurally different acetyl derivatives are possible, this reaction must take place as follows : The acetyl chloride unites with the tertiary phenyl-imido group and then separates hydrogen chloride, giving unsymmetrical acetylphenylpseudomethylthiourea (II), and the hydrochloride of phenylpseudomethylthiourea :[2]

$$H_2N-C \begin{array}{l} NC_6H_5 \\ SCH_3 \end{array} + ClCOCH_3 =$$

$$HN=C \begin{array}{l} N \begin{array}{l} C_6H_5 \\ COCH_3 \end{array} \\ SCH_3 \end{array} + \begin{array}{l} H_2N \\ Cl \end{array} C \begin{array}{l} NHC_6H_5 \\ SCH_3 \end{array}.$$

II.
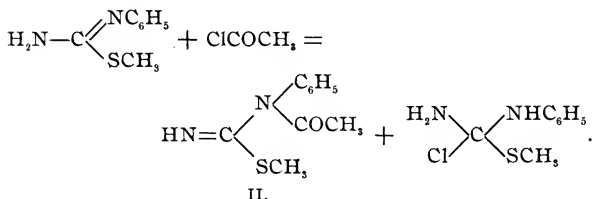
This unsymmetrical acetyl derivative has basic properties, since, on treating in ether with dry hydrogen iodide, it gives an immediate precipitate of a hydroiodide or addition-product, which can be repeatedly crystallized from alcohol. This melts at 152°.

[1] This JOURNAL, **26**, 412 (1901).

[2] The Schotten-Baumann method has been used with success for the preparation of the corresponding unsymmetrical benzoyloxygenpseudoureas by Stieglitz and McKee : This JOURNAL, **26**, 230 (1901). In the present case, owing to the unstable nature of the products, this method could not be employed.

$$\text{III.} \quad HN=C \underset{\displaystyle SCH_3}{\overset{\displaystyle N \underset{COCH_3}{\overset{C_6H_5}{<}}}{<}} + HI = \quad H_2N \underset{I}{\overset{}{>}} C \underset{SCH_3}{\overset{N \underset{COCH_3}{\overset{C_6H_5}{<}}}{<}}.$$
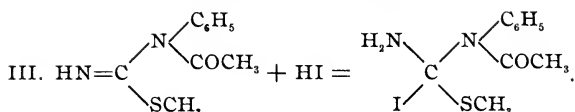
Finally, Hugerhoff's labile urea, on standing a few hours
with methyl iodide, gives a methyl iodide addition-product
that is identical in melting-point, in properties, and in fact in
every respect, with the above hydroiodide. The addition in
this case therefore takes place as follows :

$$\text{IV.} \quad H_2N—CS—N \underset{COCH_3}{\overset{C_6H_5}{<}} + CH_3I =$$

$$H_2N \underset{I}{\overset{}{>}} C \underset{SCH_3}{\overset{N \underset{COCH_3}{\overset{C_6H_5}{<}}}{<}}.$$
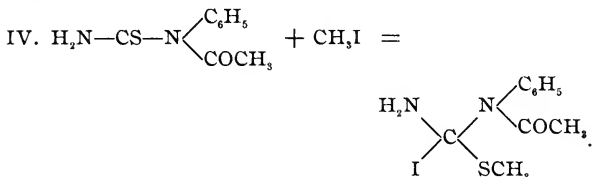
On the other hand, the hydrogen iodide addition-product
obtained from symmetrical acetylphenylpseudomethylthiourea
melts at about 116°, and it has entirely different properties from
those of the product obtained by methods III. and IV. The
following, therefore, represents the formation and structure
of this salt :

$$\text{V.} \quad CH_3CON=C \underset{SCH_3}{\overset{NHC_6H_5}{<}} + HI =$$

$$CH_3CONH \underset{I}{\overset{}{>}} C \underset{SCH_3}{\overset{NHC_6H_5}{<}}.$$
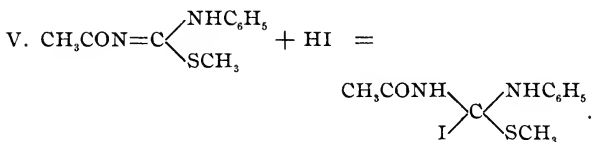
The fact that these two salts are different shows that a
molecular rearrangement does not take place in their prepa-
ration, and it excludes the possibility that the labile and stable
forms are stereochemical isomers. Were this latter assump-
tion true, one and the same hydroiodide would be formed by
all three methods.

The identity of the products formed by adding hydrogen
iodide to our unsymmetrical acetylphenylpseudomethylthio-
urea, on the one hand, and methyl iodide to Hugerhoff's

18-27

labile derivative on the other, therefore proves that the series of labile thioureas have the aryl and acetyl groups attached to the same nitrogen atom. It follows from this that the molecular rearrangement which takes place when these labile ureas are heated is as follows:

VI. $H_2N—CS—N(C_6H_5)COCH_3 \rightarrow$
$$CH_3CONH—CSN(C_6H_5)H,$$

or VII. $HN=C(SH)N(C_6H_5)COCH_3 \rightarrow$
$$CH_3CONH—C(SH)=NC_6H_5.$$
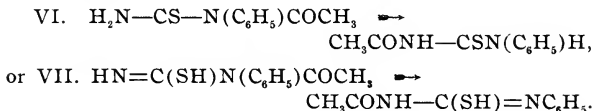
According to VI. the acetyl group and hydrogen simply change place; or, if the acetylthioureas have the pseudo form, the rearrangement may involve a migration of the acetyl group and shifting of the double bond, as shown in formula VII. At any rate, unsymmetrical acetylthioureas are transformed into symmetrical isomers on heating.

This interesting molecular rearrangement is not confined to the acylthiourea series. Dr. Treat B. Johnson and I have found that the same behavior is met with in the case of unsymmetrical acetyl- and benzoylpseudothioureas. For example, the above unsymmetrical acetylphenylpseudomethylthiourea, II., simply on melting, is transformed into the stable symmetrical acetylphenylpseudomethylthiourea, I. It follows from this that the sulphur atom takes no part in these rearrangements.[1]

The melting-points of the isomeric acetylphenylpseudomethylthioureas differ by only 2°, and curiously, the stable form has the lower melting-point, *viz.*, 82° to 83°. However,

[1] These cases, therefore, present examples of unsymmetrical amidines undergoing a metastatic change into symmetrical amidines, and the author believes we can draw the conclusion that when but one form of a "tautomeric" substance is known, it corresponds to the stable form which is produced by heating the labile acyl or alkyl derivative. The normal alkylthiocyanates undergo a molecular rearrangement into isothiocyanates, $NCSR \rightarrow RNCS$; therefore thiocyanic acid has the structure HNCS. The imidoesters are transformed into alkyl amides; the amides are derivatives of the keto form, $OC—N<$ (Wislicenus and Goldschmidt: Ber. d. chem. Ges., **33**, 1470). Since the isonitriles are converted into nitriles by simple molecular rearrangement, hydrogen cyanide should have the structure HCN. In the transformation of the substituted amidines or acylpseudothioureas the stable form is shown to be $H_2N—C(R)=NC_6H_5$, and, therefore, the question of the structure of monophenylbenzenyl and similar amidines should be decided in favor of the above, instead of the form $HN=C(R)—NHC_6H_5$ (Peckmann: Ber. d. chem. Ges., **30**, 1781 (1897)). This view will receive further attention at a later time.

in the case of unsymmetrical benzoylpseudomethylthiourea and unsymmetrical benzoylphenylpseudobenzylthiourea, the melting-points of the isomers are widely different, and the change on heating is most striking. When the first-mentioned benzoyl derivative is heated it melts at 86° to 87°, sharply and completely. If cooled and reheated, it no longer shows the slightest trace of melting at 86° to 87°, the heating having transformed the material into the stable symmetrical derivative, which melts at 104°. The latter compound was prepared by Wheeler and Merriam[1] from dimethyl benzoylimidodithiocarbonate and aniline.

This molecular rearrangement takes place even more readily than that of Hugerhoff's labile compounds, inasmuch as our labile derivatives cannot be crystallized from alcohol. In fact, even on standing in cold alcohol they pass into the stable isomers as follows :

$$HN=C(SCH_3)N(C_6H_5)COC_6H_5 \longrightarrow$$
$$C_6H_5CONH-C(SCH_3(=NC_6H_5 \quad VIII.$$
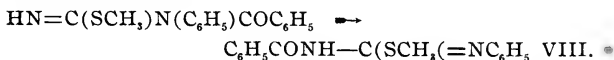
The behavior of the labile and stable acylphenylpseudothioureas with alkali is perfectly analogous to that of the corresponding acetylphenylthioureas. Labile acetylphenylpseudomethylthiourea gives acetanilide and methyl thiocyanate, the decomposition taking place as follows :

$$HN=C(SCH_3)NC_6H_5COCH_3 = NCSCH_3 + HNC_6H_5COCH_3.$$
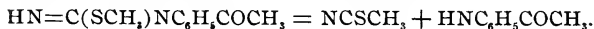
On the other hand, alkali merely dissolves the stable products, leaving no insoluble material, and no anilides are formed. On adding acid, unaltered material is precipitated. An excess of hydrochloric acid, however, redissolves the precipitates. They are, therefore, best precipitated by carbon dioxide.

The study of the molecular rearrangement described in this paper will be continued, in order to determine whether the reaction is monomolecular, involving an inner condensation according to IX., or dimolecular with the character of a saponification, X. :

[1] J. Am. Chem. Soc., **23**, 293 (1901).

$$
\underset{\text{IX.}}{\overset{\displaystyle N}{\underset{\displaystyle NC_6H_5}{RSC}}\diagdown\hspace{-0.5em}\underset{\diagup}{\overset{\diagup}{C}}\diagdown\hspace{-0.5em}\underset{\displaystyle CH_3}{\overset{\displaystyle OH}{}}}
\qquad
\underset{\text{X.}}{\overset{\displaystyle NH\quad CH_3CO.\,C_6H_5N}{\underset{\displaystyle NC_6H_5.\,COCH_3\quad HN}{RSC\diagdown\hspace{3em}\diagup CSR}}}
$$

We also wish to determine whether or not this molecular rearrangement can be accomplished in the case of other unsymmetrical thiourea derivatives, with radicals other than the acyl group, and we ask that this work be left to us.

<div align="center">EXPERIMENTAL PART.</div>

Unsymmetrical Acetylphenylpseudomethylthiourea,
$CH_3CO(C_6H_5)N—C(SCH_3)=NH$.—This was prepared by dissolving 15 grams of phenylpseudomethylthiourea[1] in a little over 150 cc. of pure dry ether, and then slowly dropping in 3.5 grams of acetyl chloride in 30 cc. of ether. During the operation the whole was cooled in a freezing-mixture. Phenylpseudomethylthiourea hydrochloride separated as a white mass, and the reaction was complete as soon as the acetyl chloride was all added. On filtering then and evaporating the ether spontaneously, beautiful, colorless prisms separated. These were about the size of grains of rice. The melting-point was found to be 85° to 86°, and a nitrogen determination gave :

	Calculated for $C_{10}H_{12}ON_2S$.	Found.
N	13.46	13.51

Behavior with Alkali.—When this material was stirred with cold dilute alkali it immediately decomposed, becoming oily, and the odor of methyl thiocyanate was noticed. On filtering and crystallizing the insoluble material from water, plates of pure acetanilide, melting sharply at 114°, were obtained. When this was mixed with acetanilide the melting-point was not changed. Carbon dioxide, when passed into the alkaline filtrate, produced no precipitate (absence of isomer).

Behavior on Heating.—Some of the material was warmed on the steam-bath for several hours. It was then treated with alkali, when nearly all dissolved, and, on passing carbon di-

[1] Bertram : Ber. d. chem. Ges., **25**, 49 (1892).

oxide into the alkaline solution, a mass of colorless, needle-like prisms separated, which proved to be symmetrical acetyl-phenylpseudomethylthiourea,

$$CH_3CONH—C(SCH_3)=NC_6H_5,$$

melting at 82° to 83°.[1]

Behavior with Hydrogen Iodide.—Dry hydrogen iodide passed into the ethereal solution gave an immediate precipitate. This was difficultly soluble in cold alcohol, but readily in hot; it separated, on cooling, in the form of colorless, four- and six-sided tables and prisms, and it melted at 152° with strong effervescence, forming a clear, red liquid. A nitrogen determination gave:

	Calculated for $C_{10}H_{13}ON_2SI$.	Found.
N	8.33	8.48

This material is, therefore, unsymmetrical acetylphenyl-pseudomethylthiourea hydroiodide,

$$CH_3CO(C_6H_5)N—C(SCH_3)INH_2.$$
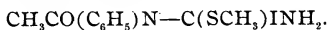
Unsymmetrical Acetylphenylthiourea and Methyl Iodide.— Hugerhoff's labile acetyl derivative melting at 139° was prepared according to his directions. It was finely pulverized and then suspended in a large excess of methyl iodide and allowed to stand for twenty-four hours; the material did not dissolve, but, nevertheless, the reaction was complete at the end of the above time. On crystallizing from alcohol it formed the same characteristic tables as the above hydro-iodide, and melted sharply at 152°, with effervescence, to a red liquid. When mixed with the above hydrogen iodide addition-product, the melting-point or temperature at which effer-vescence began was not altered.

Both these products, moreover, showed the same behavior with aqueous alkali. In the cold the material is immediately decomposed, acetanilide and methylthiocyanate being formed. There can, therefore, be no doubt that the compounds are identical. A nitrogen determination gave:

[1] Wheeler and Johnson : This JOURNAL, **26**, 412 (1901).

	Calculated for $C_{10}H_{13}ON_2SI$.	Found.
N	8.33	8.64

Symmetrical Acetylphenylpseudomethylthiourea and Hydrogen Iodide.—The symmetical pseudothiourea was prepared from dimethyl acetylimidodithiocarbonate. In regard to the preparation of this it was stated[1] in our article that only one-half of the reaction-product of dimethyl acetyldithiocarbamate, sodium ethylate, and methyl iodide consisted of the ester. This was due to the fact that the action was carried out at ordinary temperature. If conducted, however, at a temperature near 0° the entire product, almost from the first to the last drop, boils at 148° at 24 mm. pressure. This material was mixed with aniline in a little alcohol, whereupon, on standing, symmetrical acetylphenylpseudomethylthiourea melting at 82° to 83° was obtained. This was dissolved in ether, and hydrogen iodide gave a bulky precipitate, which was thoroughly washed with anhydrous ether. It melted at about 116°, with effervescence. On attempting to crystallize from alcohol it was found that the material was much more soluble than the isomeric hydroiodide, and on boiling the alcoholic solution the salt was decomposed. It could be precipitated from its alcoholic solution by ether. A nitrogen determination gave:

	Calculated for $C_{10}H_{13}ON_2SI$.	Found.
N	8.33	8.41

The behavior of this salt with alkali served to distinguish it sharply from the isomer. In dilute alkali it immediately dissolved to a clear solution, and on passing in carbon dioxide, a well crystallized mass of needle-like prisms separated, which melted sharply at 82° to 83° (symmetrical acetylphenylpseudomethylthiourea).

Symmetrical acetylphenylthiourea and methyl iodide did not react under the same conditions as the unsymmetrical derivative.

Unsymmetrical Benzoylphenylpseudomethylthiourea. — Ten grams of phenylpseudomethylthiourea were dissolved in 100

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[1] Wheeler and Johnson : This JOURNAL, 26, 192 (1901).

cc. of dry ether and to the cooled solution 4.2 grams of benzoyl chloride, in 40 cc. of ether, were slowly added. On filtering and evaporating spontaneously, a snow-white mass of needles separated, which melted at 86°. A nitrogen determination gave :

	Calculated for $C_{15}H_{14}ON_2S$.	Found.
N	10.37	10.59

The behavior with alkali is perfectly analogous to that of the labile acetyl derivative. The material, without dissolving, is converted into benzanilide and methyl thiocyanate.

Behavior on Heating.—The material melted sharply and completely at 86°, but on cooling and reheating there was no sign of melting below 90°; then up to 104° the substance melted. It was found that this labile compound could not be crystallized unchanged from alcohol. If the solution was boiled and then cooled, large, thin, colorless plates were obtained, which melted sharply at 104°, the melting-point of symmetrical benzoylphenylpseudomethylthiourea.[1]

In fact, on simply standing in cold alcohol the material undergoes this molecular rearrangement. If rapidly evaporated by means of a current of air, the alcoholic solution deposits needles of unaltered labile material, less rapid evaporation gives needles or thin prisms, and some tables, slow evaporation produces large tables, the tables being the rearranged product.

Symmetrical benzoylphenylpseudomethylthiourea, which crystallizes either in large, thin plates or tables, and melts at 104°, is readily soluble in alkali ; from this solution carbon dioxide precipitates the unaltered material in crystalline form.

Unsymmetrical Benzoylphenylpseudobenzylthiourea, $C_6H_5CO(C_6H_5)N$—$C(SCH_2C_6H_5)$=NH, by Dr. Treat B. Johnson.—In our article on acetyl and benzoylpseudothioureas[2] we described the stable form of this urea. We found that, by treating phenylpseudobenzylthiourea[3] with benzoic anhydride and crystallizing the product from alcohol, symmetrical ben-

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[1] Wheeler and Merriam : J. Am. Chem. Soc., 28, 293 (1901).

[2] *Loc. cit.*

[3] This JOURNAL, 26, 410 (1901).

zoylphenylpseudobenzylthiourea, melting at 116° to 117°, was obtained. An entirely different result was brought about when the pseudourea was treated with benzoyl chloride in ether, and the ether allowed to evaporate spontaneously. The material thus obtained, on washing with cold alcohol, melted at 92° to 92°.5. A nitrogen determination gave :

	Calculated for $C_{21}H_{18}ON_2S$.	Found.
N	8.09	8.10

When this was treated with alkali, benzanilide and benzyl thiocyanate were obtained.

When heated or crystallized from boiling alcohol, the material was transformed into symmetrical benzoylphenylpseudo-benzylthiourea, which dissolved unaltered in alkali and was precipitated by carefully adding hydrochloric acid. The stable urea dissolves in an excess of hydrochloric acid. The statement, previously made by us, that the acylpseudothio-ureas appear to have no basic properties was founded on the fact that their benzene solutions gave no precipitate with hydrogen chloride. The salts which are formed under these conditions are soluble in benzene.

NEW HAVEN, CONN., February, 1902.

XCIV.—ON SOME DOUBLE SULPHATES OF THAL-LIC THALLIUM AND CAESIUM.

BY JAMES LOCKE.

Among the most characteristic compounds formed by members of the first sub-group in the third family in the periodic system are the alums. All three of the lighter elements of the group, aluminium, gallium, and indium, yield them ; and in strict analogy to its prototypes, therefore, thallic thallium should form salts of the same nature. The general impression does seem to exist, in fact, that thallic alums have been prepared ; partly owing, perhaps, to the general tendency of chemists to assume, off-hand, a strong analogy between all the members of a family, and partly to a paper by Lepsius.[1] This investigator obtained a double sulphate of thallous and

[1] Verh. Naturforsch. u. Aerzte, **63,** [2] 103 ; Centrbl., 1891, I., 694.

thallic thallium, of the formula $Tl^I Tl^{III} (SO_4)_2$, which, he says, "is to be regarded as an anhydrous alum...., etc.," and this expression has crept into the handbooks.

There is certainly no more reason why an anhydrous double sulphate of thallium should be regarded as an alum than should a similar salt of cerium, or iridium, or any other trivalent metal. That it is so called is a very good instance of the arbitrary manner in which analogy is often found in the system when it happens to be more needed than self-evident. The double sulphates of thallic thallium with sodium and potassium are likewise anhydrous, and so far as is known, therefore, absolutely no indication of power on the part of thallic sulphate to form alums has been observed.

In view of the position of the element in the system, however, such compounds would, of course, attain considerable importance, and at my suggestion, therefore, Mr. David E. Breinig has undertaken to ascertain whether, under perhaps more favorable conditions, one could not be prepared. It has been shown by Piccini[1] that caesium yields alums far more readily than do any of the other univalent metals. My own experience, also, has shown, that while the sulphates of some of the trivalent metals, *e. g.*, iron, indium, etc., unite with most of the alkali sulphates to form salts containing less than 12 molecules of water, often more readily, in fact, than they form the alums, not one of the alum-forming trivalent metals yields with caesium more than the one hydrated salt.[2]

The failure of the sulphate of a given trivalent metal to unite with caesium sulphate to a compound of the type $CsM^{III}(SO_4)_2.12H_2O$ may therefore be taken as an almost positive indication that such element has no alum-forming power whatsoever. This we have found to be the case with thallic thallium. Its sulphate was crystallized with caesium sulphate under the most varied conditions, from both hot and cold solutions, and under no circumstances could the formation of the isometric crystals of an alum be observed. Two different hydrated double salts were obtained, and possibly a third. But they all contained much less water than is called

[1] Ztschr. anorg. Chem., **17**, 355, etc.

[2] This JOURNAL, **26**, 166.

for by a compound of the alum series. Although as far as its main purpose is concerned, therefore, the results of our investigation were entirely negative, except in that they establish the strong improbability that thallic alums are capable of existence, if it may be well to describe the salts obtained during our experiments, as a slight contribution to the literature of the thallic compounds in general.

The thallic sulphate used was prepared by treating the freshly precipitated hydroxide with the calculated quantity of concentrated sulphuric acid and adding first the desired quantity of water, and then enough more sulphuric acid to bring the salt into clear solution. To this the requisite amount of a concentrated solution of caesium sulphate was added. On mixing even a small proportion of the latter with a fairly concentrated cold solution of the thallic sulphate, a compact white precipitate at once separates out, which is very sparingly soluble in cold water, but dissolves readily upon application of heat. Recrystallization of a product obtained with equivalent quantities of caesium sulphate and thallium sulphate yielded small, well-formed, prismatic crystals, which probably belong to the rhombic system. Seen under the microscope they were almost colorless and of a characteristic hemimorphous habit. The same crystals were obtained with varying quantities of caesium sulphate, at all temperatures from 40° to 0°. The products were in all cases perfectly homogeneous, no isometric crystals at all being observed. A quantity of this salt was recrystallized from sulphuric acid solution, and after washing with more dilute acid and drying as perfectly as possible, was submitted to analysis. The various constituents were determined in separate portions. The thallium was weighed as iodide and the caesium as sulphate, after removal of the thallium by means of ammonium sulphide. The water was estimated directly, by ignition in a tube containing lead oxide. The results correspond fairly well with the formula

$$CsTl(SO_4)_2.3H_2O.$$

The somewhat high percentage of sulphuric acid found is due to the difficulty of removing the latter from the recrystallized

salt. The latter is at once decomposed by water or 95 per cent alcohol, and a considerable quantity of sulphuric acid must be present in the wash-water to prevent hydrolysis:

	Calculated for CsTl(SO$_4$)$_2$.3H$_2$O.	Found.
Cs	22.81	21.80
Tl	34.98	34.40
SO$_4$	32.95	34.21
H$_2$O	9.26	8.62
	100.00	99.03

A second salt was obtained from the mother-liquor of the above by evaporating to a high point of concentration of the sulphuric acid and allowing to cool. This body separates in the form of thin, highly lustrous plates, which, under the microscope, proved to consist of very regularly-formed rhombic plates. The crystals are so transparent that in clusters of 5 or 6 superimposed plates the edges of the undermost can readily be seen through the others. It was impossible to obtain a completely satisfactory analysis of this salt, owing to its hygroscopic nature and the difficulty of removing the concentrated acid. One product was obtained with 5.21 per cent water, and the caesium and thallium were in the ratio 1 : 1. Its composition, according to these data, would be

$$CsTl(SO_4)_2.1\tfrac{1}{2}H_2O.$$
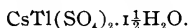
For this formula 4.86 per cent H$_2$O is required.

Incidentally to the above experiments, attempts were made to prepare an alum with chromic acid instead of sulphuric. With one exception, the observed analogy between chromates and sulphates has hitherto been confined purely to simple salts, this instance being found in the compound

$$(NH_4)_2Mg(CrO_4)_2.6H_2O,$$
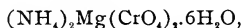
which is isomorphous with the corresponding double sulphates.

The most sparingly soluble alums being those of aluminium, solutions of aluminium chromate and caesium dichromate were crystallized together in all proportions and at various temperatures. Under no conditions

could the formation of an alum be observed. Sulphuric
acid was then added, in the hope that mixed chromate
and sulphate alum crystals might be obtained, this having
been shown by Retgers[1] to be a most delicate test for the iso-
morphism of two compounds, one of which is colored. The
small octahedrons of caesium aluminium alum which were
deposited, however, proved to be perfectly colorless, and en-
tirely free from chromium. It would seem, therefore, that, at
least within ordinary limits of temperature, chromic acid, as
well as thallic thallium, has no tendency at all to enter into
alums.

NEW HAVEN, CONN., February, 1902.

THE SULPHATES OF BISMUTH.

BY. F. B. ALLAN.

An acid sulphate of bismuth, $Bi_2O_3.4SO_3$, with 1, 3, 7, or
$10H_2O$, has recently been described by Adie.[2] He obtained
it by crystallization from sulphuric acid of greater con-
centration than $H_2SO_4.5H_2O$ ($.=52$ per cent H_2SO_4), the
amount of water in the salt depending on the concentration of
the acid and on the temperature. It has also been described
by Leist.[3]

$Bi_2O_3.3SO_3$ has been obtained by heating the acid sulphate
(Schultz-Sellac,[4] Hensgen[5]). Only double salts containing it
have been obtained in the wet way.

$5Bi_2O_3.11SO_3.17H_2O$ crystallizes from sulphuric acid of con-
centration $H_2SO_4.6H_2O$ ($=47.5$ per cent) to $H_2SO_4.12H_2O$
($=31$ per cent) [Adie].

$Bi_2O_3.2SO_3.2H_2O$ and $Bi_2O_3.2SO_3.3H_2O$ crystallize from di-
lute sulphuric acid (Leist, Heintz,[6] Luddecke,[7] Ruge[8]).

$Bi_2O_3.SO_3$ is formed by the action of water on $Bi_2O_3.2SO_3$
(Heintz, Ruge, Hensgen).

[1] Ztschr. phys. Chem., **3**, 497.
[2] Proc. Chem. Soc., 1899, p. 226.
[3] Ann. Chem. (Liebig), **160**, 29.
[4] Ber. d. chem. Ges., **4**, 13.
[5] Rec. trav. chim. Pays-Bas., **4**, 399.
[6] Pogg. Ann., **63**, 55.
[7] Ann. Chem. (Liebig), **140**, 277.
[8] J. prakt. Chem., **96**, 138.

$4Bi_2O_3.3SO_3.15H_2O$ was prepared by Leist by the repeated washing of the acid sulphate with water. Hensgen could not obtain this salt.

$3Bi_2O_3.2SO_3.3H_2O$ is obtained by heating a solution of bismuth nitrate with sodium sulphate in a closed tube at 200° to 250° (Athanasesco[1]).

In this research acid bismuth sulphate or the basic salt prepared by stirring the acid sulphate with 10 per cent sulphuric acid, was stirred with sulphuric acid solutions of different concentrations till equilibrium was reached. The apparatus used was the same as that described in this JOURNAL, **25**, 307 (1901). For that part of the series near the point at which both basic sulphates are present, the reaction was very slow and required six weeks for completion. Where the liquid contained little sulphuric acid, the composition of the solid phase was deduced from the change in the liquid, but the solids in equilibrium with the stronger acid solutions were analyzed directly, after being rubbed between porous plates. Great difficulty was found in freeing the salt from the adhering sulphuric acid, and the analyses, as a rule, show values for sulphuric anhydride which are slightly too high.

In the following table, the second column contains the composition of the liquid phases in the different bottles, at equilibrium, expressed in percentages of sulphuric acid, or with reference to a normal solution. The third column shows the composition of the solid contents :

$\dfrac{Bi_2O_3}{SO_3}$ in $Bi_2O_3.4SO_3 = 1.45$.

"   " $5Bi_2O_3.11SO_3 = 2.64$.

"   " $Bi_2O_3.2SO_3 = 2.90$.

"   " $Bi_2O_3.SO_3 = 5.80$.

Temperature 50°.

[1] Compt. rend., **103**, 171.

No.	Composition of liquid. Per cent H_2SO_4.	$\dfrac{Bi_2O_3}{SO_3}$ in solid.
1	90	1.36
2	80	1.43
3	75	1.38
4	65	1.45
5	60	1.47
6	51.4	2.21
7	47.5	2.84
8	40	2.89
9	25	2.84
10	20	2.86
11	15	2.85
12	10	2.90
	$N.H_2SO_4$.	
13	9 = 1.7	2.87
14	1.51	2.85
15	1.37	2.88
16	1.09	3.27
17	1.11	3.61
18	1.11	3.91
19	0.77	5.78
20	0.55	5.77
21	0.36	5.77
22	0.18	5.79

These results may be represented in two diagrams, in each of which the composition of the solid contents is represented by one axis, and the composition of the liquid by the other, but in the second, which includes Nos. 13 to 22, a different scale is used in representing the composition of the liquid phase:
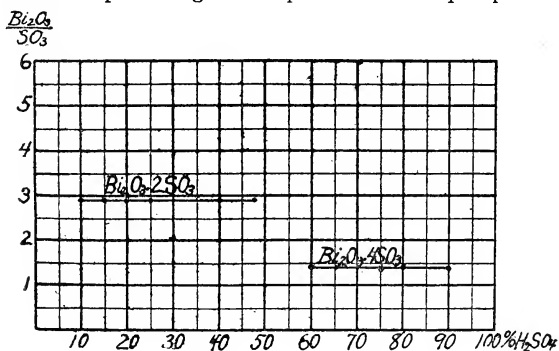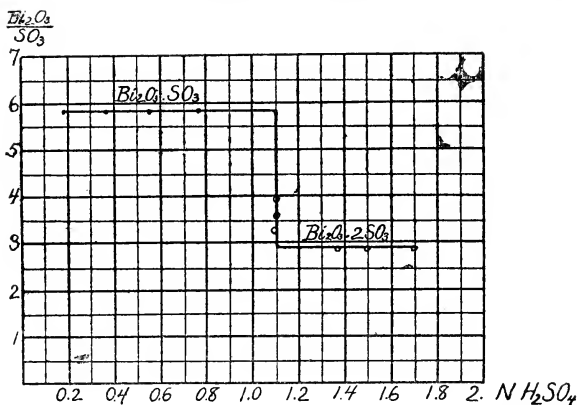
It will be seen that Nos. 1 to 5 have but one solid phase, $Bi_2O_3.4SO_3$, Nos. 7 to 15 contain $Bi_2O_3.2SO_3$, and Nos. 19 to 22 contain $Bi_2O_3.SO_3$. Nos. 16 to 18 have liquid phases of the same composition and two solid phases, $Bi_2O_3.2SO_3$ and $Bi_2O_3.SO_3$.

The salt obtained from Nos. 19 to 22 was stirred with water, at 50° for twelve days, and sulphuric acid could not be detected in the liquid.

The amount of water in the acid salt was not determined. A specimen of $Bi_2O_3.2SO_3$ dried between paper gave results agreeing with the formula $Bi_2O_3.2SO_3.2\frac{1}{2}H_2O$.

	Calculated for $Bi_2O_3.2SO_3.2\frac{1}{2}H_2O$.	Found.
Bi_2O_3	69.42	69.40
SO_3	23.87	23.90

This salt lost only a trifling amount when heated to 100°.

Summary.

1. At 50° acid bismuth sulphate is in equilibrium with sulphuric acid solutions from 51.4 per cent up, $Bi_2O_3.2SO_3.2\frac{1}{2}H_2O$ with acid solutions between 1.1 normal ($= 5.4$ per cent) and 51.4 per cent, and $Bi_2O_3.SO_3$ with acid solutions weaker than 1.1 normal.

2. $Bi_2O_3.SO_3$ is not acted on by water at 50°.

3. The salt $5Bi_2O_3.11SO_3.17H_2O$ described by Adie was not obtained.

CHEMICAL LABORATORY, UNIVER-
SITY OF TORONTO, January, 1902.

THE SOLUBILITY OF BARIUM SULPHATE IN FERRIC CHLORIDE, ALUMINIUM CHLORIDE, AND MAGNESIUM CHLORIDE.

BY G. S. FRAPS.

In working on the determination of sulphuric acid in soils, Mr. C. B. Williams, assistant chemist to the North Carolina Department of Agriculture, found that considerably more barium sulphate was obtained when the iron and aluminium had been previously precipitated from the soil solution.[1] This led to the following work.

The latest determinations of the solubility of barium sulphate which have been made are those of R. Fresenius and E. Hintz,[2] in which the solubility was determined in pure water, 2.5 and 10 per cent ammonium chloride, 2.5 per cent sodium chloride, 10 per cent nitric acid, and 10 per cent hydrochloric acid, alone, and in the presence of an excess of sulphuric acid or barium chloride.

In regard to the effect of ferric salts, aluminium salts, and magnesium salts upon its solubility, we have few data. Fresenius states that its solubility in water is increased by the presence of magnesium chloride, and Lunge[3] states that it is soluble in ferric chloride. As the precipitation of barium sulphate sometimes take place in the presence of these salts, the knowledge of its solubility is important in analytical work.

Method of Work.

The method used was similar to that adopted by R. Fresenius,[4] barium chloride being used in place of barium hydroxide.

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[1] His results are not yet published.
[2] Ztschr. anal. Chem., **35,** 170 (1896).
[3] *Ibid.*, **19,** 431.
[4] *Loc. cit.*

A solution of barium chloride was prepared, 100 cc. of which was found to give 0.0952 and 0.0945 gram barium sulphate, *i. e.*, 1 cc. = 0.95 milligram $BaSO_4$. A solution of sulphuric acid was prepared, 100 cc. of which gave 0.1206 and 0.1204 gram barium sulphate, or 1 cc. was equal to 1.2 milligrams barium sulphate.

Preliminary tests were then made upon solutions of ferric chloride, aluminium chloride, and magnesium chloride. 400 cc. of the solutions were placed in precipitating jars and sulphuric acid and barium chloride solution were added in the proper proportions to make 10 milligrams barium sulphate. The solution was allowed to stand twenty-four hours, and if no precipitate appeared 10 milligrams more of barium sulphate were added, and so on until a precipitate appeared.

More exact tests were then made, based upon the results of the preliminary tests. In making these tests, the solution was allowed to stand forty-eight hours instead of twenty-four, as it was found that precipitates sometimes appeared during the second twenty-four hours. Much smaller quantities of barium sulphate were added each time, and the very faintest trace of appearance of barium sulphate was watched for. It was found that if the stirring-rod was rubbed against the sides of the vessel the barium sulphate separated out at this point more rapidly and more readily than elsewhere, and could be easily seen. In making up the solutions of the various salts, allowance was made for the quantity of water which would probably be added with the barium chloride and sulphuric acid.

Results of Work.

The solubility of nascent barium sulphate in the solution of chlorides of different concentrations is given in the following table. Neither barium chloride nor sulphuric acid was present in excess in any case.

Solubility of Barium Sulphate.

Amount of salt per liter. Grams.	BaSO$_4$ dissolved per liter.		
	FeCl$_3$.	Milligrams in AlCl$_3$.	MgCl$_2$.
1	58	33	30
2½	72	43	30
5	115	60	33
10	123	94	33
25	150	116	50
50	160	170	50
100	170	175	50

Solubility Curves of Barium Sulphate.
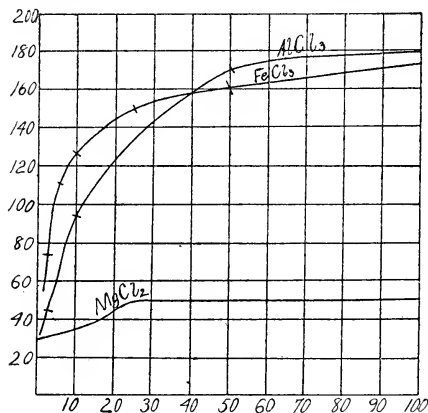
Comparing these figures with the results of Fresenius with other salts, we find that barium sulphate is much less soluble in 10 per cent ferric chloride, or aluminium chloride, than in 10 per cent nitric acid, or hydrochloric acid. It is also more readily soluble in a 10 per cent solution of ammonium chloride than in ferric chloride or aluminium chloride, of the same strength, though less soluble in 2.5 per cent ammonium chloride.

Solubility in Presence of Barium Chloride.

The solubility of barium sulphate in ferric chloride and

aluminium chloride in the presence of barium chloride in excess was tested in the same way as before. The results are as follows. In each case 12.5 milligrams barium sulphate per liter were present (5 milligrams in 400 cc.) :

With 5 grams aluminium chloride and 7.5 cc. of barium chloride (1 : 10) per liter present, the solution became turbid in an hour.

With 10 grams aluminium chloride and 20 cc. barium chloride the solution became turbid in an hour.

With 25 grams aluminium chloride and 12.5 cc. barium chloride a very faint precipitate appeared in forty-eight hours.

With 5 grams ferric chloride, 7.5 cc. barium chloride, a slight precipitate appeared in twenty-four hours.

With 10 grams ferric chloride, 20 cc. barium chloride, a slight precipitate appeared in twenty-four hours.

With 25 grams ferric chloride and 12.5 cc. barium chloride a very faint precipitate appeared in forty-eight hours.

Comparing these results with those of Fresenius, we find that, in the presence of barium chloride, barium sulphate is less soluble in ferric chloride, or aluminium chloride, than in a 10 per cent, or 2.5 per cent, solution of ammonium chloride, or in a 2.5 per cent solution of sodium chloride, or nitric acid, or hydrochloric acid.

RALEIGH, N. C., February, 1902.

I. AN INVESTIGATION OF THE FATTY OIL CONTAINED IN THE SEEDS OF LINDERA BENZOIN.

II. LAURIC ACID AND SOME OF ITS DERIVATIVES.[1]

BY CHARLES E. CASPARI.

Stillman and O'Neill[2] undertook an investigation of the fatty oil contained in the fruit of the California bay tree, *Umbellularia Californica* or *Laurus Californica*, and isolated a new acid, $C_{11}H_{22}O_2$, which they called umbellulic acid. This acid is one of the few exceptions to the general rule that of

[1] From the author's dissertation submitted to the Board of University Studies of the Johns Hopkins University, June, 1900, for the degree of Doctor of Philosophy.

[2] This JOURNAL, **4**, 206.

the higher members of the fatty acid series only those occur in nature which contain an even number of carbon atoms. This new acid differs quite markedly from the isomeric unde-cylic acid, $C_{11}H_{22}O_2$, obtained by Krafft. However, very little is known about umbellulic acid, as no work has been done on it since the publication of the article referred to above.

It was thought possible that, since the *Lindera Benzoin* belongs to the same family as the California bay tree, it might also contain umbellulic acid or some acid closely related to it, and it was with this possibility in mind that the present investigation was undertaken.

While it has not been possible to isolate umbellulic acid or indeed any acid containing an uneven number of carbon atoms, nevertheless, some interesting results have been obtained.

Lindera Benzoin, also known as *Benzoin odoriferum* and *Laurus Benzoin*, and commonly called spicewood, spicebush, or feverbush, is a bush growing to the height of 20 feet, frequently much lower, and is indigenous all over the United States. It is found chiefly in damp regions along water courses, and is quite generally used in the southern states by the country people as a remedy against fever and measles. It has a strong odor of spices and contains an ethereal oil in all of its parts.[1]

The oil of its bark and twigs has the odor of wintergreen, boils between 170° and 300°, has the sp. gr. 0.923 and contains 9 to 10 per cent of methyl salicylate. The oil from the berries contains about 4 per cent of an oil with a camphoraceous odor, the sp. gr. 0.850 to 0.855, which boils from 160° to 270°. The leaves contain about 0.3 per cent of an oil having the odor of lavender and the sp. gr. 0.888.

In this investigation only the oil from the berries has been dealt with. In the neighborhood of Baltimore, where the material was collected, the berries ripen in the middle or latter part of September, and must be gathered very soon after they ripen, otherwise they will fall to the ground and be lost in the undergrowth.

When ripe the berries have a bright-red color, are oval in shape and are about a half inch long. A half bushel of these

[1] Report of Schimmel & Co., October, 1885, p. 27, and October, 1890, p. 49.

were collected in Howard County, Maryland, and were steeped in water for several days until the outer flesh or pulp began to soften and decay. It was then comparatively easy to obtain the inner kernel entirely free from the softer pulp. The kernels were allowed to dry completely in the air. The half bushel of berries yielded about 2,500 grams of kernels.

The investigation is divided into two parts: first, the examination of the oil from the berries, and second, a thorough investigation of lauric acid, which was found in the oil as a glyceride, and of some of its derivatives.

Examination of the Oil Contained in the Berries of the Lindera Benzoin.

A few grams of the kernels were thoroughly macerated, mixed with ether, and extracted for several hours in a Soxhlet extractor. The ether was evaporated from the solution, the residue mixed with water and subjected to distillation with steam. An extremely small amount of oil distilled over, which contained all the odorous material of the oil, since the residue after distillation was entirely odorless. However, the amount of volatile oil was so very small that it was impossible to obtain enough of it from the amount of material at hand for investigation, and so the work was confined to that portion of the oil which is not volatile with water vapor. It is hoped at some later day to complete the examination of the volatile oil.

A quantitative determination of the oil contained in the seeds gave the following result:

3.2809 grams seeds yielded 1.9065 grams oil, which is equivalent to 58.10 per cent.

This result is a trifle too high, because it was impossible to prevent a small amount of the finely divided pulp from filtering through the paper thimble of the Soxhlet extractor, and this pulp was then weighed with the oil, but the error is only a very small one.

Some difficulty was experienced in obtaining a satisfactory method for extracting the oil from the seeds.

It was first attempted to extract all the material with ether in a Soxhlet extractor, but this method was unsatisfactory

for two reasons. In the first place, some of the pulp was always present in the oil, and it was practically impossible to filter it off; and in the second place, the extractors at hand were so small that it would have entailed a great loss of time to have extracted all the seeds in that way. It was then attempted to moisten the macerated pulp with ether, and express the mass in a hand press which was available. This method gave the oil free from pulp, but the yield was only about 60 per cent of what it should have been. Finally, Professor Remsen wrote to Messrs. Fritzsche Brothers, in Garfield, New Jersey, asking them whether they would extract the seeds for us. They very kindly consented to do so, and I take this opportunity of thanking them for their kindness. They expressed the seeds, and then extracted the expressed mass with petroleum ether boiling at 40° to 50°. After evaporating the petroleum ether, the extracted and expressed oils were distilled with steam for several hours, but the amount of volatile oil was so small that they did not consider it worth the trouble of isolating it. From 2130 grams of the seeds were obtained

735 grams = 34.5 per cent of expressed oil,
237 grams = 11.1 per cent of extracted oil.
Total: 972 grams = 45.6 per cent.

The product obained from Messrs. Fritzsche Brothers was a solid fat. It was yellow and quite crystalline throughout its structure. It melted at 26°. The fat is very soluble in ethyl alcohol, benzene, gasoline, and acetone, but is more difficultly soluble in anhydrous methyl alcohol. Its solution in ethyl alcohol reacts neutral towards litmus.

1.9311 grams fat require for saponification 0.5492 gram caustic potash. Hence 1 gram fat requires 284.4 milligrams caustic potash for saponification.

Volatile and Soluble Acids.—The saponified material obtained in the above determination was used for this determination. The alcohol was evaporated and the potassium salts were dissolved in water. The fatty acids were set free by dilute sulphuric acid. After diluting with water, the mixture was distilled so that 110 cc. of distillate were obtained in a

half hour. This distillate was then filtered and titrated with N/10 caustic potash, using phenolphthalein as an indicator. The amount of alkali required for neutralization was 0.998 cc. The weight of fat used was 1.9311 grams. Therefore, 2.5 grams of fat would require 1.29 cc. N/10 caustic potash to neutralize the volatile and soluble acids contained in it. Hence the Reichert number is 1.29. Another determination gave the value 1.34.

These results show that the percentage of volatile and soluble acids obtained from the fat is very small, and they doubtless consist of small amounts of capric acid, $C_{10}H_{20}O_2$, which was later found in the fat as the glyceride, and which is volatile with steam and slightly soluble in water.

While the distillation was in progress in determining the Reichert number, it was noticed that a small amount of some material came over, which was insoluble in water and solid at ordinary temperatures. Some of this material was collected and dissolved in alcohol, and this solution reddened blue litmus paper. The solution was heated to boiling, and to it was added a hot solution of lead acetate in alcohol. Very soon fine, delicate needles, clustering together in rosettes, appeared, and when the solution had cooled these were filtered off, washed well with water and with alcohol, and dried over calcium chloride. Analysis of the salt yielded the following results:

I. 0.1460 gram salt gave 0.0757 gram $PbSO_4$.
II. 0.3128 gram salt gave 0.1581 gram $PbSO_4$.

	Calculated for $Pb(C_{12}H_{23}O_2)_2$.	Found.	
		I.	II.
Pb	34.17	35.34	34.52

The barium salt of the same acid was made by treating a boiling alcoholic solution of the acid with a boiling alcoholic solution of barium acetate. The salt was washed, dried over calcium chloride, and analyzed with the following results:

I. 0.2629 gram salt gave 0.1157 gram $BaSO_4$.
II. 0.2203 gram salt gave 0.0971 gram $BaSO_4$.

	Calculated for $Ba(C_{12}H_{23}O_2)_2$.	Found.	
		I.	II.
Ba	25.64	25.87	25.92

From the above analytical results it would seem that the acid was lauric acid, which is difficultly volatile with water vapor and which is insoluble. However, through subsequent work this conclusion was shown to be wrong, and the explanation of the above results will be given further on.

To make sure that the barium salt mentioned above was a salt of lauric acid alone, it was subjected to fractional crystallization from water, in which it is quite insoluble.

Two or three grams of the barium salt were boiled with two liters of water. A portion of it dissolved and was filtered boiling hot. Immediately crystals began to separate out, and after about fifteen minutes these were filtered off, dried, and analyzed.

0.1836 gram salt gave 0.0805 gram $BaSO_4$.

	Calculated for $Ba(C_{12}H_{23}O_2)_2$.	Found.
Ba	25.65	25.75

When the above filtrate had cooled to the temperature of the room, more crystals had separated out. These were filtered off, dried over calcium chloride, and analyzed.

0.1340 gram salt gave 0.0611 gram $BaSO_4$.

	Calculated for $Ba(C_{12}H_{23}O_2)_2$.	Calculated for $Ba(C_{11}H_{21}O_2)_2$.	Calculated for $Ba(C_{10}H_{19}O_2)_2$.	Found.
Ba	25.65	27.06	28.64	26.84

The filtrate from the second crop of crystals was concentrated considerably by evaporation, and when the solution had cooled crystals again separated out. After drying over calcium chloride they were analyzed.

0.2582 gram salt gave 0.1237 gram $BaSO_4$.

	Calculated for $Ba(C_{10}H_{19}O_2)_2$.	Found.
Ba	28.64	28.20

Next, the crystals which were found to contain 26.84 per cent of barium were dissolved in boiling water, and the solution was allowed to cool to the temperature of the room. The crystals which separated out were dried and analyzed.

0.2306 gram salt gave 0.1017 gram $BaSO_4$.

	Calculated for $Ba(C_{12}H_{23}O_2)_2$.	Found.
Ba	25.65	25.95

The filtrate from these crystals was evaporated down, and, upon cooling, a second crop of crystals separated out. These were likewise dried and analyzed.

0.1994 gram salt gave 0.0959 gram $BaSO_4$.

	Calculated for $Ba(C_{10}H_{19}O_2)_2$.	Found.
Ba	28.64	28.32

Finally, that portion of the original barium salt which was insoluble in boiling water was boiled with more water and went completely into solution. It had not dissolved before because there had not been enough water present. Almost as soon as boiling ceased crystals began to separate out quite rapidly, and these were filtered off while the solution was still quite hot. After drying over calcium chloride they gave the following result upon analysis :

0.2589 gram salt gave 0.1114 gram $BaSO_4$.

	Calculated for $Ba(C_{12}H_{23}O_2)_2$.	Found.
Ba	25.65	25.33

The filtrate from these crystals, when cooled down to the temperature of the room, did not deposit enough crystals for an analysis, and when concentrated considerably by evaporation, and cooled, not enough material for analysis separated out.

This fractional crystallization of the barium salt offers very strong evidence in favor of the fact that the material which is volatile with steam and insoluble in water, obtained when the mixed acids derived from the fat are distilled with steam, consists not of lauric acid alone, but of lauric and capric acids. Of the first three fractions obtained, the first one approximates very closely to barium laurate, the third one to barium caprate, while the second one gives an analysis which agrees very well with that demanded by barium undecylate, $Ba(C_{11}H_{21}O_2)_2$, but the second one, when redissolved and subjected to fractional crystallization, can be resolved into two salts whose barium content agrees very well with that of barium laurate and barium caprate. Finally, that portion of the original barium salt which remained undissolved, when it was first boiled with water, dissolved completely when more water was added, and

upon crystallization yielded practically only barium laurate. This can be explained only if barium laurate and barium caprate were originally present. The first time the barium salt was boiled with water, a large part of the barium laurate and all of the barium caprate went into solution, because barium caprate is much more soluble in water than barium laurate, and the residue which dissolved completely when boiled again with water consisted entirely of barium laurate, and did not dissolve at first on account of its great insolubility in water.

It now seems clear why the lead and barium salts described on page 295 gave analytical results agreeing so well with those of barium laurate and lead laurate. Evidently, in each case, lead acetate and barium acetate had been added in quantities insufficient to precipitate the acids completely. Only the lead and barium laurates crystallized out with perhaps a very little of the caprates, because the caprates are so much more soluble than the laurates in alcohol, as well as in water.

The fractional crystallization of the barium salt of the mixed acids, and the subsequent liberation of the free acids from their separated salts does not offer a very expedient method for the separation of the pure acids, because such an enormous amount of water is required to dissolve the original barium salts. Hence it was thought best to saponify the fat, liberate the free acids, and subject them to fractional distillation under diminished pressure. In this way it is possible to separate the individual acids quite thoroughly.

Accordingly, about 250 grams of the fat obtained from Fritzsche Brothers were saponified with an alcoholic solution of potassium hydroxide (66 grams to the liter). After the alcohol was distilled from the saponified material, there was left a dark-brown, pasty mass, which consisted of the potassium salts of the fatty acids, together with any glycerol which might have been present in the fat in the form of glycerides. This dark residue was dissolved completely in cold water, and from this solution the free acids were precipitated by means of dilute sulphuric acid. They are solid at ordinary temperatures, and float on the aqueous solution. The entire mass was heated on the water-bath until the acids had melted and had collected completely at the surface. Upon cooling, the

acids formed a solid cake, which could be easily lifted off from the aqueous solution. This aqueous solution was filtered, neutralized with potassium hydroxide, and evaporated almost to dryness. The residue was extracted five times with absolute alcohol, and this alcoholic solution was afterwards examined for glycerol. The fatty acids were heated on the water-bath for ten to twelve hours in order to dry them as much as possible before distilling them.

The apparatus used for distillation under diminished pressure was that recommended by Anschütz. It consisted of two distilling bulbs, the side tube of one fitting into the neck of the other, which was the receiver. The side tube of the receiver was connected with a manometer, which in turn was connected with an ordinary filter-pump. Only rubber stoppers and very thick-walled rubber tubing were used in making connections. A capillary tube, through which a small current of air was constantly kept passing, dipped under the surface of the boiling liquid rendering the ebullition more regular, and preventing any liquid which was not first vaporized from passing over into the receiver. The distilling bulb was never more than one-third filled, and was placed in an iron dish, the bottom of which was covered with fine asbestos, so that the bulb could not come in contact with the metal, and then heat was applied to the iron dish. The temperature of the air-bath was never allowed to rise more than 40° higher than the temperature of the vapor in the distilling bulb. No condenser tube was necessary, since the acids boiled so high that the side tube of the distilling bulb was sufficiently long to condense all the vapors.

Under 11 to 15 mm. pressure, the acids which had been dried on the water-bath, began to boil at 150°, and from the first distillation two fractions were collected, from 150° to 170° and from 170° to 185°. The portion boiling above 185° was reserved for examination later on. These two fractions were then redistilled and three fractions were collected under 12 to 14 mm. pressure, from 154° to 157°, from 157° to 166°, and from 166° to 187°. In the last fraction most of the distillate came over at about 168°. During the distillation the temperature of the air-bath varied from 190° to 220°. The first and

third fractions contained approximately equal volumes, while the volume of the intermediate fraction was much smaller than that of the first or third. These three fractions were colorless when liquid and white when solid, with a decidedly crystalline structure. The barium salts of the acids in the first and third fractions were made by bringing together a boiling alcoholic solution of the acid with a concentrated boiling solution of barium acetate in about 50 per cent alcohol. After being washed with alcohol and with water and dried in the air, these salts were analyzed for barium with the following results:

Fraction boiling from 154° to 157° under 12 to 14 mm. pressure.

    I. 0.2144 gram salt gave 0.1025 gram $BaSO_4$.

    II. 0.2321 gram salt gave 0.1107 gram $BaSO_4$.

	Calculated for $Ba(C_{10}H_{19}O_2)_2$.	Found. I.	II.
Ba	28.64	28.15	28.08

Fraction boiling from 166° to 187° under 12 to 14 mm. pressure.

    I. 0.2935 gram salt gave 0.1281 gram $BaSO_4$.

    II. 0.2918 gram salt gave 0.1274 gram $BaSO_4$.

	Calculated for $Ba(C_{12}H_{23}O_2)_2$.	Found. I.	II.
Ba	25.65	25.69	25.70

From these results the conclusion may be drawn that the fraction boiling from 154° to 157° consisted mainly of capric acid with perhaps a very little lauric acid, and that the fraction boiling from 166° to 187° consisted of quite pure lauric acid.

In order to obtain a purer capric acid, the fraction boiling from 154° to 157° was redistilled, together with the intermediate fraction mentioned above, which, under the same pressure, boiled from 157° to 166°. From this distillation three fractions were obtained, the first boiling from 156° to 157° under 15 mm. pressure, the second boiling from 150° to 154° under 10 to 11 mm. pressure, and the third from 157° to 169° under 13 mm. pressure. The first fraction had by far the largest volume, while the second and third fractions each had

a volume which was much smaller than that of the fraction boiling from 157° to 166° under 10 to 12 mm. pressure. These facts show that this last-mentioned fraction was composed of a lower and a higher boiling portion. The analyses below show that it consisted of a mixture of capric and lauric acids.

The barium salts of the three new fractions were made exactly as those described above, and upon analysis gave the following results for barium :

Fraction boiling from 156° to 157° under 15 mm. pressure.

I. 0.2007 gram salt gave 0.0965 gram $BaSO_4$.

II. 0.2315 gram salt gave 0.1115 gram $BaSO_4$.

	Calculated for $Ba(C_{10}H_{19}O_2)_2$.	Found. I.	II.
Ba	28.64	28.31	28.35

Fraction boiling from 150° to 154° under 10 to 11 mm. pressure.

I. 0.2656 gram salt gave 0.1254 gram $BaSO_4$.

II. 0.2017 gram salt gave 0.0948 gram $BaSO_4$.

	Calculated for $Ba(C_{10}H_{19}O_2)_2$.	$Ba(C_{12}H_{23}O_2)_2$.	Found. I.	II.
Ba	28.64	25.65	27.76	27.67

Fraction boiling from 157° to 169° under 13 mm. pressure.

I. 0.2240 gram salt gave 0.0997 gram $BaSO_4$.

II. 0.2573 gram salt gave 0.1148 gram $BaSO_4$.

	Calculated for $Ba(C_{10}H_{19}O_2)_2$.	$Ba(C_{12}H_{23}O_2)_2$.	Found. I.	II.
Ba	28.64	25.65	26.20	26.27

Thus, the first fraction consists of practically pure capric acid, the second fraction of capric acid with a little lauric acid, and the third fraction of lauric acid with a very much smaller amount of capric acid. From this it appears evident that no acid of the formula $C_{11}H_{22}O_2$ was present, a conclusion also arrived at from the evidence presented by the fractional crystallization of the barium salts of the mixed acids, when the barium salt containing 26.84 per cent of barium, the percentage of barium in the barium salt of $C_{11}H_{22}O_2$ being 27.06, was resolved into barium caprate and barium laurate.

A small portion of the residue boiling above 185° under 11 to 15 mm. pressure was dissolved in chloroform and treated

with bromine water. The color of the bromine disappeared immediately, showing the presence of some unsaturated acid. To test whether this acid was formed during the distillation by decomposition from lauric and capric acids, some of the original fat was treated in solution in chloroform with bromine water, and again the color disappeared immediately, showing that the unsaturated compound was present as such in the original fat. The high-boiling residue was distilled under 10 mm. pressure. Up to 218° very little distillate was obtained, and this was doubtless impure lauric acid, as it solidified almost immediately. From 218° to 225° a very appreciable amount of a clear liquid distilled over, and above 225° the mass carbonized. The distillate which came over between 218° and 225° melted at 13°, the melting-point of oleic acid being given as 14°. A hot alcoholic solution of the acid, which did not redden blue litmus paper, another characteristic of oleic acid, was treated with ammonium hydroxide and barium chloride, and filtered hot. Upon cooling, a voluminous white crystalline precipitate separated out, which, upon analysis, gave the following results :

I. 0.2372 gram salt gave 0.0786 gram $BaSO_4$.
II. 0.2147 gram salt gave 0.0710 gram $BaSO_4$.

	Calculated for $Ba(C_{18}H_{33}O_2)_2$.	I.	Found. II.
Ba	19.63	19.51	19.47

These results point to the conclusion that the acid boiling from 218° to 225° under 10 mm. pressure is oleic acid. Krafft and Nordlinger[1] give 223° as the boiling-point of oleic acid under 10 mm. pressure. Another piece of evidence also showed that oleic acid is contained in the fat. It is well known that lead oleate is soluble in ether, while the lead salts of the saturated acids are not. Accordingly, the potassium salts of the mixed acids from the fat were treated in aqueous solution with a solution of lead acetate. A copious, white, creamy precipitate was immediately thrown down, and was filtered off and dried as well as possible in the air. It was then extracted with ether several times, and the solution in ether was evaporated down considerably when a yellowish

[1] Ber. d. chem. Ges., **22**, 819.

crystalline mass separated out. This mass was recrystallized from ether, and was finally obtained as a white crystalline powder, which melted at about 80° to a yellow liquid. Upon analysis for lead it gave the following results :

I. 0.2437 gram salt gave 0.0953 gram $PbSO_4$.

II. 0.2156 gram salt gave 0.0845 gram $PbSO_4$.

	Calculated for $Pb(C_{18}H_{33}O_2)_2$.	I.	II.
		Found.	
Pb	26.88	26.69	26.75

These two pieces of evidence—one from the acids after distillation, the other from the crude acids—leave little doubt that oleic acid is contained in the original fat.

It will be remembered that when the fat had been saponified and the acids set free, the aqueous filtrate from the acids was neutralized with potassium hydroxide, evaporated almost to dryness, and that the residue was extracted several times with absolute alcohol. This alcoholic solution was then examined for glycerol. The alcohol was evaporated off and there was left a thick, viscous liquid, quite sweet to the taste. This was heated to 170° in order to drive off all traces of alcohol and water. Portions of this residue were heated in a test-tube with about twice their mass of acid potassium sulphate when the disagreeable penetrating vapors of acrolein were evolved, proving that the thick liquid above mentioned was glycerol.

It is clear from the results here given that the fatty oil or fat of the seeds of the *Lindera Benzoin* consists of a mixture of the glycerides of capric, lauric, and oleic acids. No quantitative determinations of the amount of each acid present were made, but the lauric acid is present in largest proportion.

LAURIC ACID AND SOME OF ITS DERIVATIVES.

Lauric acid was discovered in 1842 in Liebig's laboratory by Marsson.[1] He obtained it by saponifying the fat contained in laurel berries, and called it laurostearic acid. The acid with which he worked melted at 42° to 43°. Sthamer[2] obtained lauric acid by saponification of the fat contained in

[1] Ann. Chem. (Liebig), **41**, 329.
[2] *Ibid.*, **53**, 390.

pichurim beans from South America. His acid melted at
43°. A few years later Görgey,[1] during an extensive investi-
gation of cocoanut oil, found that it contained lauric acid.
Capric and caprylic acids were also present, and he separated
the three acids by fractional crystallization of their barium
salts. He described lauric acid very much as Marsson and
Sthamer had done, and said it melted at 42° to 43°. Heintz[2]
obtained lauric acid, which melted at 43°.6, from whale fat.
In 1867, Oudemans[3] found lauric acid as a constituent of
Fangkallak fat obtained from the *Cylicodaphne sebifera*, of Java.
Oudemans,[4] in 1863, prepared and described several of the
salts of lauric acid. He did not state the source or the melt-
ing-point of his acid, and since many of his results differ con-
siderably from those obtained with the lauric acid from the
seeds of *Lindera Benzoin*, it is questionable whether Oude-
mans was dealing with perfectly pure lauric acid. As most
of the work on lauric acid was done more than forty years
ago, it seemed desirable that some of the work should be re-
peated with the aid of modern improvements in chemical
methods.

The method of obtaining lauric acid from the seeds of *Lin-
dera Benzoin* has already been described. The acid melts at
42° and boils at 166° under 10 to 11 mm. pressure. It is very
soluble in alcohol, from which it can be crystallized in warty
crystals, which have a satin luster. It is practically insolu-
ble in water. In alcoholic solution it turns blue litmus paper
red. Upon analysis the acid gave the following results :

I. 0.2432 gram acid gave 0.6398 gram CO_2 and 0.2662
gram H_2O.

II. 0.2314 gram acid gave 0.6083 gram CO_2 and 0.2557
gram H_2O.

	Calculated for $C_{12}H_{24}O_2$.	Found.	
		I.	II.
C	71.91	71.75	71.69
H	12.10	12.17	12.27

In order to be sure that this acid is identical with that ob-

[1] Ann, Chem. (Liebig), **66**, 290.
[2] *Ibid.*, **92**, 294.
[3] Ztschr. Chem., 1867, p. 256.
[4] J. prakt. Chem., **89**, 206.

tained by Krafft[1] from laurel oil, from whose results those here given differ somewhat, a half kilogram of laurel oil was purchased from Dodge and Olcott, in New York, which yielded about 10 per cent of lauric acid by saponification and distillation under diminished pressure. This acid melted at 42° and boiled at 166° under 11 mm. pressure, and was in all respects identical with that obtained from the seeds of the *Lindera Benzoin*. Krafft said that his acid melted at 43°.5.

Of the sources of lauric acid thus far discovered, the seeds of the *Lindera Benzoin* yield it most abundantly and with comparatively little difficulty.

The Chloride of Lauric Acid, $C_{11}H_{23}.CO.Cl.$—The chloride[2] of the acid was made by treating the melted acid with a little more than the calculated amount of phosphorus trichloride and heating the mixture on the water-bath for fifteen or twenty minutes, until the action was complete. In this reaction only the chloride of the acid and phosphorous acid are formed. The latter sinks to the bottom of the dish as a rather viscous liquid, so that the chloride can be poured from it very easily. In order to purify this crude chloride, it was subjected to distillation under diminished pressure, and after one distillation it yielded the following analytical results:

I. 0.3772 gram chloride gave 0.2447 gram AgCl.
II. 0.2264 gram chloride gave 0.1474 gram AgCl.

	Calculated for $C_{11}H_{23}.COCl$	Found. I.	II.
Cl	16.21	16.04	16.09

The chloride is decomposed slowly by the moisture in the air, and must hence be well protected from the air. It is also decomposed very quickly by alcohol. According to Krafft[3] it boils at 142°.5 under 15 mm. pressure and melts at —17°. That which gave the above results boiled at 145° under 18 mm. pressure, and remained liquid when cooled down to —17°.

The Amide of Lauric Acid, $C_{11}H_{23}.CONH_2.$—The amide of lauric acid was made according to the method for the general preparation of acid amides recommended by Aschan.[4] It was

[1] Ber. d. chem. Ges., **12**, 1664.
[2] *Ibid.*, **31**, 2344.
[3] *Ibid.*, **17**, 1378.
[4] *Ibid.*, **31**, 2344.

his method that was used in making the acid chloride. The chloride was added, drop by drop, to an excess of a well-cooled, concentrated solution of ammonia, which was constantly stirred. The amide was precipitated out immediately, as it is insoluble in water. It was crystallized several times from 50 per cent alcohol until its melting-point remained constant after three crystallizations. The amide crystallizes in very fine, feathery, white needles, which, when dry, have a very fluffy appearance with a satin luster. It melts sharply between 98° and 99°. Upon analysis it gave the following results :

0.1689 gram amide gave 0.4492 gram CO_2 and 0.1938 gram H_2O.

	Calculated for $C_{11}H_{23}.CONH_2$.	Found.
C	72.26	72.53
H	12.67	12.73

0.3202 gram amide gave 0.0228 gram N.

	Calculated for $C_{11}H_{23}.CONH_2$.	Found.
N	7.02	7.13

The nitrogen was determined as ammonia by the Kjeldahl method.

The amide of lauric acid has been made only once before, and then by Krafft.[1] He does not give any analyses of his product nor does he say how he purified it. His amide melted at 102°.

The Anilide of Lauric Acid, $C_{11}H_{23}.CO.NH.C_6H_5$.—This was made by adding the chloride, drop by drop, to an emulsion in water of twice the calculated amount of aniline required. The product of the reaction was crystallized several times from 50 per cent alcohol, and finally it melted constantly before and after two crystallizations at 76°.5. The anilide crystallizes quite well in long, feathery, fluffy, white needles, resembling finely shredded asbestos. It was analyzed for nitrogen by the Kjeldahl method with the following result :

0.2548 gram anilide gave 0.0133 gram N.

	Calculated for $C_{11}H_{23}.CO.NH.C_6H_5$.	Found.
N	5.10	5.20

[1] Ber. d. chem. Ges., **15**, 1729.

The o-Toluide of Lauric Acid, $C_{11}H_{23}.CO.NH.C_6H_4.CH_3$.—This forms very fine, light, white needles, which melt at $81°.5$. A determination of nitrogen yielded the following result by the Kjeldahl method.

0.2496 gram toluide gave 0.0119 gram N.

	Calculated for $C_{11}H_{23}.CO.NH.C_6H_4.CH_3$.	Found.
N	4.84	4.78

The amide, anilide, and toluide of lauric acid resemble each other very closely in appearance and in their solubility. They are all insoluble in water and easily soluble in 95 per cent alcohol. The best menstruum from which to crystallize them is 50 per cent alcohol.

Barium Laurate, $Ba(C_{12}H_{23}O_2)_2$.—Barium laurate was made by bringing together a boiling solution of lauric acid in 95 per cent alcohol and a boiling solution of barium acetate in 50 per cent alcohol. Almost immediately after mixing the two solutions the crystals of barium laurate separated out. They consist of very fine, white needles, arranged in the form of rosettes. These, when dry, have a luster resembling that of mother of pearl or of fish scales.

Barium laurate is very difficultly soluble in water and in alcohol, and does not melt when heated to $260°$. It yielded the following analytical results for barium :

    I. 0.4751 gram salt gave 0.2061 gram $BaSO_4$.
    II. 0.4351 gram salt gave 0.1897 gram $BaSO_4$.

	Calculated for $Ba(C_{12}H_{23}O_2)_2$.	I.	II.
		Found.	
Ba	25.64	25.54	25.66

Oudemans[1] describes barium laurate as amorphous, while as a matter of fact it is quite crystalline.

Strontium Laurate, $Sr(C_{12}H_{23}O_2)_2 + H_2O$.—Strontium laurate was made by mixing a boiling solution of lauric acid in 95 per cent alcohol with a boiling solution of strontium acetate in 50 per cent alcohol. Before the solution had cooled crystals of strontium laurate separated out. These consisted of fine, white needles, which clustered together, but did not have the pearly luster of barium laurate. Strontium laurate

[1] J. prakt. Chem., **89**, 206.

is as insoluble in water as barium laurate and nearly as insoluble in alcohol. It decomposes, without melting, at about 240° and contains 1 molecule of water of crystallization.

I. 0.2177 gram salt gave 0.0076 gram H_2O.
II. 0.2236 gram salt gave 0.0077 gram H_2O.

	Calculated for $Sr(C_{12}H_{23}O_2)_2 + H_2O$.	Found. I.	II.
H_2O	3.57	3.51	3.48

I. 0.2101 gram anhydrous salt gave 0.0790 gram $SrSO_4$.
II. 0.2159 gram anhydrous salt gave 0.0811 gram $SrSO_4$.

	Calculated for $Sr(C_{12}H_{23}O_2)_2$.	I.	Found. II.
Sr	18.02	17.96	17.93

Calcium Laurate, $Ca(C_{12}H_{23}O_2)_2 + H_2O$.—Calcium laurate was made like the barium and strontium salts. It is much more soluble in alcohol than either of these salts and crystallizes in very short, delicate, white needles, which cannot be distinctly seen without the aid of a pocket lens. The crystals contain one molecule of water of crystallization and melt at 182° to 183°.

I. 0.2145 gram salt gave 0.0075 gram H_2O.
II. 0.2027 gram salt gave 0.0070 gram H_2O.

	Calculated for $Ca(C_{12}H_{23}O_2)_2 + H_2O$.	Found. I.	II.
H_2O	3.94	3.49	3.45

This salt is efflorescent, and this fact accounts for the somewhat low results obtained in the determination of water of crystallization.

I. 0.2070 gram anhydrous salt gave 0.0657 gram $CaSO_4$.
II. 0.1957 gram anhydrous salt gave 0.0613 gram $CaSO_4$.

	Calculated for $Ca(C_{12}H_{23}O_2)_2$.	I.	Found. II.
Ca	9.12	9.33	9.21

Acid Magnesium Laurate, $Mg(C_{12}H_{23}O_2)_2.C_{12}H_{24}O_2$.—This salt was obtained by treating a hot alcoholic solution of lauric acid with a hot neutral alcoholic solution of magnesium acetate. It was expected that the normal magnesium laurate would be formed, but in two instances the acid salt was obtained, and it was impossible to obtain the normal salt. This

case of magnesium forming an acid salt seems to be an isolated one. The salt is the most soluble salt of lauric acid, with the exception of potassium and sodium laurates. It crystallizes most readily from 50 per cent alcohol in very fine, white needles, which melt at 74° to 75°. Analyses for magnesium gave the following results:

I. 0.2012 gram salt gave 0.0377 gram $MgSO_4$.
II. 0.2591 gram salt gave 0.0486 gram $MgSO_4$.

	Calculated for $Mg(C_{12}H_{23}O_2)_2.C_{12}H_{24}O_2$.	I.	Found. II.
Mg	3.91	3.79	3.79

Oudemans[1] described the normal magnesium laurate, $Mg(C_{12}H_{23}O_2)_2$, and said it contained 3 molecules of water of crystallization. Strange to say, this salt melted at 75°, the melting-point of the acid salt described above. Oudemans did not state how he prepared his magnesium laurate.

Zinc Laurate, $Zn(C_{12}H_{23}O_2)_2$.—Zinc laurate was made as the previous salts were. It is moderately soluble in alcohol, and crystallizes in delicate white needles, arranged in the form of rosettes. It also has a pearly or satin luster like that of the barium salt.

I. 0.2067 gram salt gave 0.0365 gram ZnO.
II. 0.2209 gram salt gave 0.0388 gram ZnO.

	Calculated for $Zn(C_{12}H_{23}O_2)_2$.	I.	Found. II.
Zn	14.09	14.18	14.07

This salt was dried in the air and contained no water of crystallization. Oudemans[2] describes a zinc laurate to which he gave the formula $Zn(C_{12}H_{23}O_2)_2 + H_2O(?)$. This melted at 80°. The salt described above melts at 127°.

Copper Laurate, $Cu(C_{12}H_{23}O_2)_2$.—Copper laurate was made just as the previously described salts were. It separates as a light bluish-green, microscopically crystalline powder. It is very difficultly soluble in alcohol and insoluble in water. When heated, it gradually turns darker, and finally assumes a dark green color.

[1] *Loc. cit.*
[2] *Loc. cit.*

I. 0.2048 gram salt gave 0.0349 gram CuO.

II. 0.2110 gram salt gave 0.0359 gram CuO.

	Calculated for $Cu(C_{12}H_{23}O_2)_2$	Found. I.	II.
Cu	13.76	13.62	13.59

Oudemans[1] described a copper laurate, $Cu(C_{12}H_{23}O_2)_2$, which he said melted at 90°, while the above-described salt does not melt when heated to 220°.

Lead Laurate, $Pb(C_{12}H_{23}O_2)_2$.—Lead laurate was made like the other salts. It is insoluble in water, but may be crystallized from alcohol. It crystallizes in delicate white needles, which have a pearly luster. They melt at 101°. Oudemans[2] described his lead laurate as being amorphous, while the salt here described forms definite crystals with comparatively little difficulty.

I. 0.2757 gram salt gave 0.1382 gram PbSO₄.

II. 0.2580 gram salt gave 0.1294 gram PbSO₄.

	Calculated for $Pb(C_{12}H_{23}O_2)_2$.	Found. I.	II.
Pb	34.18	34.22	34.23

Manganese Laurate, $Mn(C_{12}H_{23}O_2)_2$.—Manganese laurate was prepared as the other salts were. It is insoluble in water, but is soluble in alcohol. It separates out from its solution as a very pale pink, microscopically crystalline powder. The crystal form could not be determined. It melts at 76°, and contains no water of crystallization. Oudemans[3] described a manganese laurate melting at 75°, and containing x molecules of water of crystallization.

I. 0.2202 gram salt gave 0.0724 gram MnSO₄.

II. 0.2327 gram salt gave 0.0761 gram MnSO₄.

	Calculated for $Mn(C_{12}H_{23}O_2)_2$.	Found. I.	II.
Mn	12.13	11.97	11.91

Cobalt Laurate, $Co(C_{12}H_{23}O_2)_2 + H_2O$.—Cobalt laurate was made as the other salts were and is quite soluble in alcohol, but insoluble in water. It forms delicate, pale-red needles, which melt at 52°, and then assume a dark-violet color. The

[1] *Loc. cit.*
[2] *Loc. cit.*
[3] *Loc. cit.*

cobalt laurate described by Oudemans[1] contained one molecule of water of crystallization, but melted at 75°.

I. 0.2211 gram salt gave 0.0078 gram H_2O.

II. 0.2070 gram salt gave 0.0074 gram H_2O.

	Calculated for $Co(C_{12}H_{23}O_2)_2 + H_2O$.	Found. I.	II.
H_2O	3.79	3.53	3.57

I. 0.2133 gram anhydrous salt gave 0.0716 gram $CoSO_4$.

II. 0.1996 gram anhydrous salt gave 0.0666 gram $CoSO_4$.

	Calculated for $Co(C_{12}H_{23}O_2)_2$.	Found. I.	II.
Co	12.89	12.77	12.71

REPORT.

The Oxygen Bases.

In the conception of oxygen—or oxonium—bases, there has been presented to chemists the introduction to what promises to be one of the most interesting chapters in the history of chemical theory, as well as one which bids fair to be far-reaching in its consequences. It is the purpose of this paper to put together in the form of a review the principal contributions to the subject which have thus far appeared.

The conception was perhaps first hinted at by Mendeléeff as early as 1871, and was used by Friedel in 1875 to account for the compound of methyl ether with hydrochloric acid. He also used it to explain the suboxides of copper and silver, and considered it the basis of water of crystallization. Two years later van 't Hoff was led by the consideration of methyl ether to much the same conclusion, and in 1882 Armstrong expressed himself as a believer in the quadrivalence of oxygen. In 1888 Heyes[2] held that one of the oxygen atoms in the superoxides is quadrivalent, and ascribed the tendency to polymerization of aldehydes, cyanates, and other similar compounds to the same cause. A similar idea was used by Meldola, Schroeder, Brühl, and perhaps others, but it was not till 1899 that the conception of quadrivalent oxygen was forced upon chemists by experimental evidence.

In the summer of that year a paper was read by Collie and Tickle[3] before the Chemical Society of London on the salts of

[1] *Loc. cit.*

[2] J. F. Heyes: The Tetravalence of Oxygen, Phil. Mag., [5], **25**, 221, 297 (1888).

[3] J. Chem. Soc. (London), **75**, 710 (1899).

dimethylpyrone. These salts are compared with those of di-
methylpyridone, and the conclusion drawn that the oxygen
atom in the pyrone must play the same part as the nitrogen
atom in the pyridone. This assumes the quadrivalence of
oxygen, and also that certain of its compounds have a basic
character, due to its presence. Such compounds are analo-
gous to the ammonium, phosphonium, sulphonium, and iodo-
nium bases, and may be called oxonium bases. They are de-
rivatives of the hypothetical oxonium hydroxide, OH_3OH.
In favor of this hypothesis the authors mention the fact that
ethers frequently form so-called double compounds with the
halogen acids, such as dimethyl ether hydrochloride, diethyl
ether hydriodide, and they also put in this category ethyl per-
oxide.

A few months later, a paper by Kehrmann[1] on the constitu-
tion of the oxazine dyestuffs was read before the German
Chemical Society. In it the author makes use of the sugges-
tion of Collie and Tickle to account for the structure of the
diaminophenoxazine and diaminophenthiazine salts. The
structure of these compounds would, therefore, be represented
by the following :
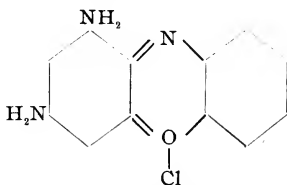
Diaminophenazoxonium   Diaminophenazthionium
chloride.   chloride.
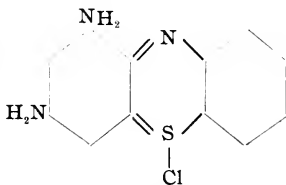
It is, of course, conceivable that it is the nitrogen atom,
rather than the oxygen and the sulphur atom, which plays
the part of the base, but a comparison of these compounds
with diamidophenylphenazine as to color and absorption spec-
tra seems to render this improbable. Several analogous azoxo-
nium and azthionium salts have been described by Kehrmann[2]
during the present year.

The contribution to this subject which has attracted the
most wide-spread attention of chemists is the notable paper by
Baeyer and Villiger,[3] on the basic properties of oxygen,
which appeared in the *Berichte* for September 28th. After re-

[1] Ber. d. chem. Ges., **32,** 2601 (1899).

[2] *Ibid.*, **34,** 1623, 4170 (1901).

[3] *Ibid.*, **34,** 2679 (1901).

viewing various classes of compounds of oxygen which have been noted in the past as forming compounds with acids, which seem to be of the nature of salts, and referring to the work of Collie and Tickle, as being in every particular verified by them, they announce as a general proposition that the simple oxygen atom, in every form in which it appears throughout organic chemistry, is capable of forming salts ; that not only in specially favorable circumstances, as Collie and Tickle thought, is it possible to obtain well-characterized salts, but with a few exceptions in every case provided only that the proper acids and the appropriate conditions are selected. The acids used in the preparation of the salts of Baeyer and Villiger were generally hydroferrocyanic, hydroferricyanic, and hydrocobalticyanic. In a few instances phosphotungstic and chlorplatinic acids were used. While a few oxygen compounds gave well-characterized salts with the simpler acids, in almost all cases far better and surer results were obtained with the complex acids. The cyanic acid reagents were prepared by precipitating the potassium salts with concentrated hydrochloric acid and filtering off the potassium chloride. Salts were formed with various members of the following classes of oxygen compounds : ethers, ethylene oxide, and cineol, primary, secondary, and tertiary alcohols, esters, aldehydes, ketones of all classes. No compounds with acids were obtained, though one of acetic acid is known. Perhaps the best results were obtained with cineol and with the ketones.

That these salts are not compounds of bivalent oxygen in the ordinary sense of the valence theory was shown by a careful study of the hydrochloride of dibenzalacetone, which is not a chlorhydrine of the formula

$$C_6H_5.CH : CH.C(OH)Cl.CH : CH.C_6H_5,$$

but has rather the formula

$$\overset{\displaystyle HCl}{\underset{\displaystyle C_6H_5.CH : CH.CO.CH : CH.C_6H_5.}{|}}$$

In favor of the theory that the oxygen bases are to be explained by the quadrivalence of oxygen, Baeyer cites the fact that the same influences which increase or diminish the basicity of nitrogen affect similarly the basicity of oxygen, and the same is true to a limited extent of sulphur. This is shown by the following table :

NH$_3$	OH$_2$	SH$_2$
base	neutral	acid
N(C$_2$H$_5$)$_3$	O(C$_2$H$_5$)$_2$	S(C$_2$H$_5$)$_2$
strong base	weak base	neutral
N(C$_2$H$_5$)$_4$OH	O(C$_2$H$_5$)$_3$OH	S(C$_2$H$_5$)$_3$OH
very strong base	hypothetical base	base

While the entrance of a positive group like alkyl renders the oxygen of the neutral water basic, this is not the case with negative groups like phenyl. Phenol, benzophenone, and similar compounds represent a class of oxygen compounds which form no salts. This is in complete accord with the character of nitrogen compounds, for in triphenylamine the basic quality of nitrogen has entirely disappeared. The basic character of oxygen is most noticeable in those compounds in which there is a double linkage between oxygen and carbon. This raises the question, which Baeyer does not attempt to answer, as to whether these compounds are not to be accounted for by the theory of residual affinity, using ideas which have been suggested by Armstrong,[1] Nef, Thiele, and others.

In the number of the *Berichte* following that in which Baeyer and Villiger's article appeared, Werner[2] takes up the work of Kehrmann, but develops it by avoiding the presence of nitrogen atoms in the molecule. The simplest compounds prepared were the perbromide and the ferric chloride double salt of xanthydrol, formed by the reduction of xanthone. Xanthydrol he considers to be a pseudoxanthoxonium base,
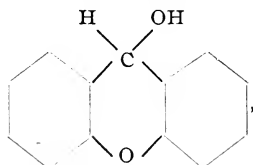
while its salts are derived from the true xanthoxonium base,
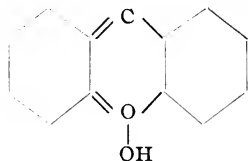
[1] Proc. Chem. Soc., 1901, 246.
[2] Ber. d. chem. Ges., **34**, 3300 (1901).

The compounds are better developed in the case of several analogous substances, which seem to leave little doubt of their structure, if they are to be accounted for by the valence theory. Such are the base formed by the reduction of benzal-β-dinaphthyl oxide, of which both the anhydride and the alcoholate of the pseudo base were formed, and the base from dixanthylene.
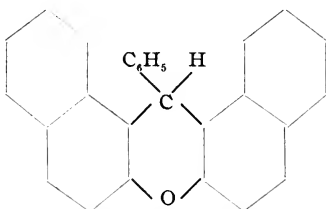
Benzal-β-dinaphthyl oxide.
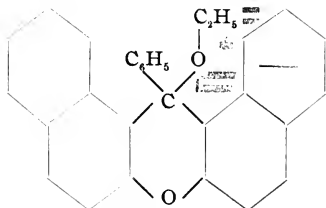
Alcoholate from pseudo base.
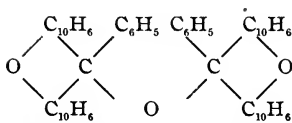
Anhydride from pseudo base.
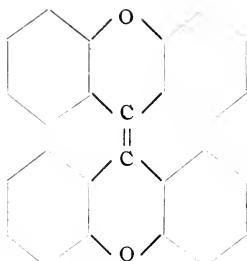
Dixanthylene.
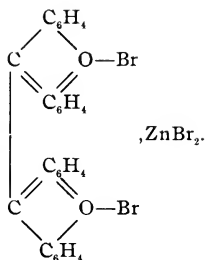
Zinc bromide double salt of di-
xanthoxonium bromide.

Werner also prepared similar derivatives containing sul-
phur in the place of oxygen and gives to these two classes
the names of "carboxonium" and "carbothionium" salts.
Werner looks upon the pyrone salts as being of analogous
constitution, differing here somewhat from Baeyer and Collie.[1]
According to Werner these are paraoxypyroxonium salts,
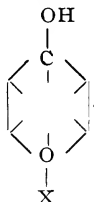
He also shows that pyrone itself is capable of forming salts.

In the same number of the *Berichte*, Rosenheim and Stell-
mann[2] describe a number of double compounds of antimony
pentachloride, including several with different classes of oxy-
gen compounds. Such are $SbCl_5,CH_3.CHO$, $SbCl_5,C_6H_5.CHO$,
$SbCl_5,(CH_3)_2.CO$, $SbCl_5,C_6H_5.CO_2.C_2H_5$, $2SbCl_5,3C_6H_5.CO.Cl$,
and $2SbCl_5,3CH_3CO.NH_2$. In the light of the oxygen bases
these compounds possess a peculiar interest, especially in view
of the fact that Rosenheim found that antimony chloride also
forms double compounds with the organic acids, which is not
the case with the complex inorganic acids with which Baeyer
and Villiger worked.

In the next number of the *Berichte*, Baeyer and Villiger[2]

[1] Ber. d. chem. Ges., **34**, 3612 (1901).

[2] *Ibid.*, **34**, 3377 (1901) ; Cf. also Rust : *Ibid.*, **30**, 2828 (1897).

take exception to the formula which Werner proposed for the pyrone salts, on the ground that there is no evidence of the presence of a hydroxyl group. He also expresses doubt as to whether the oxonium bases really correspond to the ammonium compounds, or are to be rather considered as molecular compounds. He calls attention to the resemblance which the salt-forming character of the oxygen compounds in general bears to that of the nitriles, which are ordinarily considered to have no basic properties. This is, however, not strictly the case, for the nitriles not only form compounds with tin tetrachloride and similar chlorides, but Baeyer shows that with the cyanic acids most of the nitriles tested form well-defined compounds which closely resemble those formed under similar circumstances with the oxygen compounds.

In a late number of the *Berichte*,[1] Kehrmann and Wentzel apply the ideas in the previous papers of Kehrmann to the constitution of Gomberg's triphenylmethyl, considering it as diphenylphenylenemethane, in which the para carbon atom of the phenylene group is bivalent, and like oxygen, under similar circumstances, plays the part of a base. When this carbon atom unites with the elements of hydrochloric acid, it becomes quadrivalent, and there is formed the isomeric yellow triphenylchlormethane. If this diagnosis is correct, we have here an instance of a ' carbonium' base.
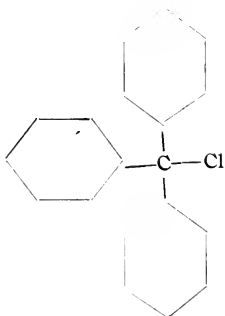
Colorless triphenylchlormethane.   Yellow triphenylchlormethane.
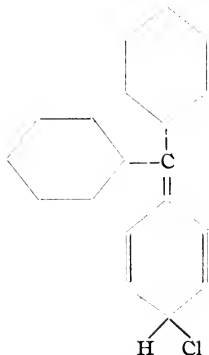
[1] Ber. d. chem. Ges., **34**, 3815 (1901).
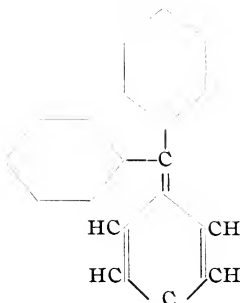
Gomberg's triphenylmethyl, a " car-
bonium" base.

In the same number of the *Berichte*, Hewitt[1] utilizes the
oxonium theory as a prop to his theory of the cause of fluo-
rescence.

Still more recently, Walker[2] has made an examination of
dimethyl- and tetramethylpyrone by physico-chemical meth-
ods.   Measuring their catalyzing effect upon methyl acetate,
he finds that their basicity is practically the same as that of
urea, dimethylpyrone being a little stronger base and tetra-
methylpyrone a little weaker.   He also finds that the hydro-
chlorides of these compounds are hydrolyzed in aqueous solu-
tion to about the same extent as the hydrochloride of urea.
He further shows, however, that, contrary to the statement of
many text-books, ethylene oxide is by no means a strong base,
but that its property of precipitating iron, aluminium, and
magnesium hydroxides from solutions of their chlorides is due
to the tendency of these salts to hydrolysis in aqueous solu-
tion.

Of the latest contributions to the subject, the most impor-
tant is that of Walden,[3] who, after a historical review of the
earlier work, gives the results of a series of physico-chemical
experiments upon dimethylpyrone.   (1) Violuric acid dis-
solved in a solution of dimethylpyrone shows no immediate
increase of colored ions, showing that in this case di-
methylpyrone has no decided tendency to form a salt, or
that its salt with violuric acid is completely hydrolyzed.
(2) From the influence of dimethylpyrone upon the birotation
of grape-sugar, it appears that, if basic at all, it is a decidedly

    [1] Ber. d. chem. Ges., **34,** 3819 (1901).
    [2] *Ibid.,* **34,** 4115 (1901).
    [3] *Ibid.,* **34,** 4185 (1901).

weaker base than aniline. (3) From the distribution coefficient of dimethylpyrone between water and benzene it appears that the picrate exists in concentrated aqueous solution, but is easily decomposed on dilution, even in the presence of an excess of the dimethylpyrone. (4) From the depression of the freezing-point the dissociation of dimethylpyrone is somewhat greater than that of pure water, that is, it is a somewhat stronger base than water. (5) In solution in liquid sulphur dioxide, dimethylpyrone is a relatively good electrolyte, corresponding in this particular to the tertiary nitrogen bases in the same solution. In acetonitrile it is an exceedingly weak electrolyte, but in the presence of tribromacetic acid, which likewise conducts very poorly, the solution increases decidedly in conductivity. This must be due to the formation of a salt. In water dimethylpyrone is a very poor conductor, and comparison shows that it is a weaker base than aniline but a stronger base than urea.

Conductivity experiments with dimethylpyrone and sodium hydroxide show that it is an amphoteric electrolyte, and the conclusion is drawn that this compound is in fact also a weak acid, capable of forming hydrogen ions as well as hydroxyl ions. In closing, Walden calls attention to the fact that oxygen must now be added to the long list of amphoteric elements, which are capable of forming both acids and bases, and suggests a similar possibility in the case of the halogens, as may be true with hypochlorous acid, which, while not conducting electricity, nevertheless forms salts with bases and reacts with acids.

From its first inception the theory of valence has undergone successive modifications and developments which have left it to-day very unlike the early conception. Regarding some of the elements, we have come to admit that they can have almost any valence, according to circumstances. Such is the case with manganese and ruthenium. In other cases we try to adhere to the idea of perissads and artiads, though here, as in the instance of sulphur and the halogens, we must admit an occasional exception. In a few cases, as hydrogen, the alkali metals, oxygen, and carbon, valence has been regarded as fixed, although there are a few notable stumbling blocks, such as carbon monoxide. Given any desired flexibility to the valence theory, it is, of course, possible to account for the structure of any compound.

But with all its changes and developments, our views of valence are far from flexible. We do not give up a single one of our valence ideas without a struggle. The quadrivalence and sexivalence of sulphur, the quinquivalence of nitrogen

were only accepted after a prolonged contest. The idea of the quadrivalence of oxygen is logical, is thoroughly in harmony with the properties of the oxygen group, and yet it will be generally accepted by chemists only when it is recognized as being the only possible way of accounting for many different compounds.

We cling to the theory of valence because we recognize that there is truth in it, but at the same time we recognize its insufficiency by making only a limited use of it. It accounts satisfactorily for the structure of most of our simpler compounds, it has been a wonderful and tolerably safe guide in the domain of organic chemistry, yet even in these two cases it is applicable with strictness only to gases where we know the weight of the molecule. In liquids we cannot be sure of it ; in solution we know not what becomes of it when the ions are dissociated ; in solids we can use it only by analogy. It is in solids, too, that the conception of valence most conspicuously breaks down. Between ammonium salts, double salts, such stable compounds as the platinum tetrammine bases, and the efflorescent decahydrate of sodium carbonate, we can bridge every step with intermediate compounds. In a limited field valence represents a quantitative truth ; in a larger field it is like a scaffold, which more or less closely keeps to the outline of the structure, and is correspondingly useful didactically in gaining a conception of the structure itself. We are yet lacking in knowledge of the chemical affinity of the atom from a quantitative standpoint.

The importance of the oxygen bases does not lie in the question of the possible quadrivalence of the oxygen atom, but rather in that oxygen is brought still more closely into line with nitrogen, phosphorus, sulphur, and iodine in the development of base-forming properties, when united to negative organic groups.   JAS. LEWIS HOWE.

WASHINGTON AND LEE UNIV.,
    LEXINGTON, VA.,
        Dec. 30, 1901.

AMERICAN

CHEMICAL JOURNAL

THE CALCULATION OF ATOMIC WEIGHTS.

By F. W. Clarke.

In the ordinary discussion of ratios relative to atomic weights, different results may be obtained by varying the method of computation. This is due to the fact that the ratios as measured are not absolute, but subject to errors, which should be, but are not usually, distributed. In most cases the tendency is to accumulate all errors, accidental or systematic, upon the constant which is last determined, a procedure which is obviously unscientific. Take, for example, the ratio

$$CaF_2 : CaSO_4,$$
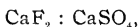
upon which our knowledge of the atomic weight of fluorine chiefly depends. In the actual measurement certain errors of observation occur; the data are reduced with assumed values for the atomic weights of calcium, sulphur, and oxygen, which are themselves, to a greater or less extent, inexact, and all of these inaccuracies are brought together in the final result of calculation. If oxygen be taken as the standard of atomic weights, and therefore not subject to error, the atomic weight of fluorine will contain the error of the experiment,

21–27

plus the errors in the atomic weights of calcium and sulphur ; and whether these compensate one another or not we have no means of knowing. Moreover, each error exerts its maximum effect, whose extent can hardly be estimated.

It is generally agreed, with but few dissenting voices, that the work of Stas upon some of the more fundamental atomic weights, is as accurate as the present resources of experimental chemistry can make it. And yet, even here, discrepancies exist which the ordinary method of calculation fails to reconcile. The ratios measured by Stas have been discussed by various writers, especially by Stas himself, by Ostwald, by Thomsen, and by Van der Plaats, and the results of the several computations vary with the method of calculation. Van der Plaats,[1] in particular, has illustrated this fact by making two calculations, giving the ratios equal weight in one (A), and weight inversely proportional to the squares of their probable errors in the other (B). In the following table the various results of the reductions appear :

	Stas.	Ostwald.	Thomsen.	Van der Plaats (A).	Van der Plaats (B).
Ag	107.930	107.9376	107.9299	107.9202	107.9244
Cl	35.457	35.4529	35.4494	35.4516	35.4565
Br	79.952	79.9628	79.9510	79.9407	79.9548
I	126.850	126.8640	126.8556	126.8445	126.8494
Na	23.043	23.0575	23.0543	23.0453	23.0443
K	39.137	39.1361	39.1507	39.1414	39.1403
N	14.044	14.0410	14.0396	14.0421	14.0519
S	32.074	32.0626	32.0606	32.0576	32.0590
Li	7.022	7.0303	7.0307	7.0273	7.0235
Pb	206.926	206.911	206.9042	206.9089	206.9308

The differences thus shown are slight, but in the case of bromine they amount to more than two in the second decimal place, an uncertainty greater than is commonly recognized. It is an uncertainty which affects all other determinations depending upon the atomic weight of bromine as an antecedent factor, and which ought to be appreciably diminished. With sulphur and nitrogen the divergencies are proportionately even greater.

Now, bearing in mind that the so-called determination of

[1] Compt. rend., **116**, 1362.

atomic weights is nothing more than the accurate measurement of chemical ratios, let us consider how the latter are to be treated. In the case first cited, the ratio between calcium fluoride and calcium sulphate, the usual method of calculation, is evidently defective, and yet, with existing data, it is the only practicable mode of procedure. With adequate data the ratio should contribute to our knowledge of at least three atomic weights, those of fluorine, calcium, and sulphur, its errors of observation being divided into three parts and not concentrated upon a single factor. That is, the ratio should be combined with other ratios in such a manner that several atomic weights might be simultaneously computed, all errors being so distributed as to reduce their influence to a minimum. With some groups of ratios calculations of this sort are already possible, and Van der Plaats' reduction of Stas' determinations is a good illustration of my meaning. In this case 23 ratios, involving the atomic weights of 10 elements, were combined into one group of normal equations, and the latter were then solved once for all. The method followed was the well-known method of least squares, and that is the only process which satisfies all conditions. Given enough data of sufficient accuracy, and the method of least squares is applicable to the problem in question, with insufficient evidence or doubtful measurements no solution is satisfactory. The mathematical operations are well understood ; it is for the chemist to furnish suitable material to which they may be applied.

In order to illustrate more fully the foregoing considerations, I have combined 30 ratios, involving the atomic weights of silver, chlorine, bromine, iodine, nitrogen, sodium, and potassium, into 7 normal equations, in which the constants named appear as the unknown quantities. The ratios are given on pages 53 and 70 of my ''Recalculation of the Atomic Weights,''[1] and contain, in addition to the work of Stas, determinations by Berzelius, Penny, Pelouze, Marignac, Dumas, Gerhardt, Maumené, Turner, Millon, Huntington, Richards, Ramsay and Aston, Hardin, Thomsen, and Hibbs. In short,

[1] Smithsonian '' Constants of Nature,'' Part V., 1897.

all determinations of the ratios in question, made up to 1897, are included in the discussion, in order that the effect of such a combination may distinctly appear. The basis of calculation, the standards of reference, are $O = 16$ and $H = 1.0079$, these values being taken as known. Personally, I prefer the hydrogen unit as a starting point, but in the present case the results are to be compared with those of other computers, as previously cited.

To show the method of calculation, let me first take one or two ratios separately. For instance, the ratio

$$Ag : Br :: 100 : 74.080$$

may be written $100\ Br = 74.080\ Ag$, when the symbols Br and Ag represent the two atomic weights respectively. So, also, the ratio

$$KClO_3 : O_3 :: 100 : 39.154$$

becomes in linear form

$$39.154\ K + 39.154\ Cl = 2920.608.$$

From 30 equations of this kind the 7 normals are constructed, each ratio contributing toward the establishment of each atomic weight represented in it. In this way errors of measurement are divided up and distributed, and even systematic errors find their influence diminished.

If all of the 30 ratios were equal in value and importance, the formation of the normals would be a comparatively simple matter, but such is not the case. Some are very exact, others are more than doubtful, and weight must be assigned accordingly. The rigorous rule is to give each measurement weight inversely proportional to the square of its probable error, and as the latter is given in every case, the rule has been applied. Only, instead of multiplying each equation by its weight, which would give coefficients of excessive size, I have divided them by suitable factors and so reduced the coefficients to manageable dimensions. The principle is unchanged, but its mode of application is somewhat unusual. The same result, however, is reached in the end, and the element of personal judgment is entirely eliminated from the discussion. Each

ratio weights itself, regardless of any preferences upon my part.

Now, taking the regular method of least squares, the 30 equations, after weighting, reduce to the following normals, seven equations containing the seven unknown quantities:

(1) $+5251.3245$ Ag -6726.5755 Cl -599.0278 Br -143.1342 I
-1238.429 N -1871.5887 Na -4417.7167 K $= 28800.227$

(2) -6726.5755 Ag $+12014.6535$ Cl -24.7694 Br -2.8347 I
$+471.803$ N $+3146.9379$ Na $+6758.0443$ K $= 41302.978$

(3) -599.0278 Ag -24.7694 Cl $+716.8553$ Br $+156.250$ N
$+204.082$ Na $+27.72$ K $= -230.712$

(4) -143.1342 Ag -2.8347 Cl $+129.2642$ I $+0.5536$ K $=$
868.704

(5) -1238.429 Ag $+471.803$ Cl $+156.250$ Br $+2954.376$ N
-35.1434 Na -334.7707 K $= -76872.85$

(6) -1871.5887 Ag $+3146.9379$ Cl $+204.082$ Br -35.1434 N
$+3319.6292$ Na $= 1919.906$

(7) -4417.7167 Ag $+6758.0443$ Cl $+27.72$ Br $+0.5536$ I
-334.7707 N $+6748.573$ K $= 24505.141$

A glance at these equations is enough to indicate some of their deficiencies. The first two only are complete; in the others eight terms are missing. In the fourth equation, which represents iodine, the terms corresponding to sodium, bromine, and nitrogen are absent, and even potassium is represented by a coefficient which is ridiculously small. Many other coefficients are smaller than they should be, and this indicates the inadequacy of some of the data. To be really satisfactory, no one of the 49 coefficients should be wanting, and all should be reasonably large. Moreover, every coefficient should represent data drawn from more than one ratio, and in too many instances this is not the case. Were Stas' data alone considered, the normals would be still more incomplete, even though the outcome of the solution might be considered better.

Upon solving the 7 normal equations the following values are obtained:

		Ag 107.9525		
Cl	35.4521		N	14.0527
Br	79.9687		Na	23.0636
I	126.8663		K	39.1573

These, except in the case of chlorine, are considerably higher than any of the values given in the table of reductions derived from the work of Stas, and yet they are not so inconsistent with the latter as they might appear to be at first sight. From the new atomic weights we can compute the value of each one of Stas' ratios, and so compare the result with the measurements which he actually made. This is done in the following table, which gives in each case the lowest and highest determination by the great Belgian.

Ratio.	Stas.		Calculated.
	Lowest.	Highest.	
$KClO_3 : O_3$	39.1527	39.162	39.149
$AgClO_3 : O_3$	25.078	25.081	25.078
$AgBrO_3 : O_3$	20.349	20.351	20.346
$AgIO_3 : O_3$	16.972	16.9761	16.972
$Ag : Cl$	32.841	32.849	32.840
$Ag : Br$	74.079	74.083	74.078
$Ag : I$	117.529	117.543	117.520
$Ag : KCl$	69.099[1]	69.1249	69.114
$Ag : KBr$	110.332	110.361	110.354
$Ag : NaCl$	54.2054	54.2093	54.205
$Ag : NaBr$	95.4383	95.4426	95.440
$Ag : NH_4Cl$	49.592	49.602	49.592
$Ag : NH_4Br$	90.823	90.8317	90.830
$Ag : AgNO_3$	157.463	157.510	157.481
$AgNO_3 : KCl$	43.864	43.885	43.886
$KCl : KNO_3$	135.638	135.655	135.654
$NaCl : NaNO_3$	145.443	145.469	145.458

In ten cases out of the seventeen the calculated ratios fall within the limits of variation shown by the experiments of Stas; in six cases they are lower than his lowest, and in only one case is the result too high. In no case is the divergence large, and in most instances it is remarkably small. My conclusion from all of these considerations is, that although the new figures should not replace the accepted values for the several atomic weights, they are not to be lightly disregarded. They serve to exemplify the ultimate method of calculation, and to show that the data need reinforcement by additional determinations, which should complete the normals

[1] Early work, supplanted by later and better measurements.

and raise the weak coefficients to adequate magnitude. When that is done, when, say 50 ratios are available instead of 30, then will the method of least squares be fully applicable to the problem, and its use will give the most probable results. To this end, ratios based upon analyses of sodium bromate, iodate and iodide, potassium bromate and iodate, and ammonium iodide, are especially desirable. Other ratios connecting chlorine, bromine, and iodine with one another are also much needed and should not be difficult to determine. For example, the ratio $AgClO_3 : AgBr$ ought to be easy of measurement, and also the reverse ratio $AgBrO_3 : AgCl$.

If the oxygen-hydrogen ratio be considered the base line in our system of atomic weights, then the determination of the 7 constants now under consideration might be compared to a primary triangulation. For this purpose no accuracy is too high, no refinement of details too laborious. If the atomic weights of carbon and sulphur should be included in the scheme, giving 9 normal equations for solution, the range of possibilities would be much increased and the results of the discussion could be made more satisfactory. With existing data, 44 ratios, good and bad, are now available, and their distribution in the normals can be seen in the following table. Here each horizontal line represents the left-hand side of one equation, and each figure indicates the number of ratios which would influence a given coefficient :

	Ag.	Cl.	Br.	I.	N.	Na.	K.	C.	S.
Ag	31	14	6	4	7	3	5	7	3
Cl	14	20	1	1	9	5	6	–	1
Br	6	1	7	–	1	1	2	–	–
I	4	1	–	5	–	–	2	–	–
N	7	9	1	–	13	2	3	1	–
Na	3	5	1	–	2	7	–	1	1
K	5	6	2	2	3	–	10	–	–
C	7	–	–	–	1	1	–	11	1
S	3	1	–	–	–	1	–	1	4

That is, the normal for silver would be formed from 31 ratios containing silver, 14 containing chlorine, etc. The other equations would all be incomplete, 24 terms being absent, and 18 more being affected only by single ratios. To

supply the 24 and to improve the 18 is the experimental part of the problem, and this is not so great a task as it might seem to be at a first glance. For example, suppose that the ratio AgCNS : AgI were capable of measurement. Its errors of observation would be divided between 5 elements, 8 missing coefficients would be supplied, and 25 coefficients in all would be affected. Merely to fill the gaps in the equations, therefore, is easy; to fill them properly is a more weighty question. To this end, 40 or 50 new ratios ought to be carefully determined, giving a system of ratios containing from 80 to 100 in all. For one chemist so great a labor would be hardly possible, but by cooperation between several workers the task might be performed, and in something like reasonable time. The methods of manipulation, the precautions to be observed, the difficulties to be encountered, are all well known, and that consideration helps to simplify the problem. Stas and Marignac have laid the foundations, and with their recorded experience to guide us we should be able to build the structure higher without excessive difficulty.

RESEARCHES ON THE OXIDES OF TUNGSTEN.

BY E. T. ALLEN AND V. H. GOTTSCHALK.

Of all the different oxides of tungsten which nave been described only two, WO_2 and WO_3, are of established composition. Formulas for at least half a dozen others have been proposed. Thus, Malaguti prepared a blue substance to which he assigned the formula W_2O_5, by heating tungstic oxide in dry hydrogen by means of an alcohol lamp.[1] Von Ulsar asserted that the compound obtained by heating tungstic trioxide strongly in hydrogen was W_3O_8. Gmelin obtained a blue compound by reducing tungstic trioxide in a current of carbon monoxide, to which Von Ulsar assigned the formula W_4O_{11},[2] though Desi was unable to get a homogeneous product in this way.[3]

By oxidizing metallic tungsten with strong sulphuric acid

[1] Ann. chim. phys., [2], **60**, 272 (1835).
[2] Graham-Otto : "Lehrbuch der Chemie," Vol. II., p. 1161.
[3] J. Am. Chem. Soc., **19**, 230.

under various conditions, Desi[1] obtained several substances which he considered chemical individuals having the formulas WO, W_4O_3, W_2O_3, and W_5O_9. These substances, like all the oxides previously referred to, were blue or bluish in color.

It was in the hope of clearing up some of these uncertainties that the present investigation was undertaken. None of the products under consideration can be sublimed or otherwise purified, consequently there is danger of being misled by mixtures. The rapid oxidation to which those which are prepared by wet methods are subject, constitutes another difficulty in their investigation, Finally, so far as known, none of them forms salts ; therefore, the formulas have to be deduced from analysis. And, since the ratio between tungsten and oxygen is large ($184 : 16$), the difference in the percentage of the elements demanded by such compounds as W_mO_n and $W_{m+1}O_{n+3}$ is correspondingly small. We have overcome these difficulties, in part, by using pure materials, washing the products out of contact with air, analyzing them without drying, and using pretty large portions for analysis. Such mixtures as result from incomplete reactions we have avoided by treating our products with successive portions of reagent.

In establishing our formulas we have also been aided by certain theoretical considerations. Thus far we have experimented only on the action which reducing agents exert on tungstic acid. This compound is much more difficult to reduce than chromic or molybdic acid.[2] In alkaline (tungstate) solution it may be boiled with grape sugar, hydroxylamine,[3] or even metallic aluminum, without undergoing any reduction. Suspended in hot concentrated hydrochloric acid, it is stable toward hydroxylamine, oxalic acid, or alcohol. Even in sealed tubes, at 200° C., the last-named reagent effected no change in the appearance of the tungstic acid, but yielded only ethyl chloride. A solution of sulphurous acid, saturated at a low temperature, may be heated to 200° C. in

[1] J. Am. Chem. Soc., **19**, 213.
[2] Regarding the reduction of tungstic acid in the dry way, see Ehrenfeldt : J. Am. Chem. Soc.. **17**, 381.
[3] Hydroxylamine forms a compound to be described later.

sealed tubes, with tungstic acid, without reducing more than traces in the upper surface layer.[1]

Nascent hydrogen, liberated from acids by the action of metals, reduces it, but since the final product seems to be metallic tungsten, this reagent did not seem to promise well for the preparation of a pure oxide. In stannous chloride and hydriodic acid, however, we found reagents well adapted to our purpose.

Reduction of Tungstic Acid with Stannous Chloride.

Stannous chloride reduces tungstic acid to a fine, dark-blue, insoluble substance. The tungstic acid merely requires to be heated on the water-bath with an excess of acidified stannous chloride solution until the color indicates that the change is complete. In our earlier experiments we poured off the reagent at this stage and repeated the reduction, but analyses of the substance showed that this was unnecessary. Three or four grams of tungstic acid is easily reduced by 20 to 25 cc. of stannous chloride solution, which may be prepared by dissolving 8 grams tin in 25 cc. concentrated hydrochloric acid. A 100 cc. Erlenmeyer flask, closed by a one-hole stopper provided with a Bunsen valve, is a convenient reaction vessel, since it serves to keep the substances out of contact with air. The product must be washed in hydrogen or carbon dioxide. A cylinder was made by cutting off the lower third of a wide-mouthed bottle, about $2\frac{1}{2}$ inches in diameter, and grinding down the edge. The smaller end was closed by a perforated stopper, through which passed the stem of the funnel which was enclosed by the cylinder. Through a second hole in this stopper passed the conducting tube for carbon dioxide (hydrogen, if used, should of course be introduced at the top). The top of the cylinder was closed by a one-hole stopper, which supported a small dropping-funnel.[2] To prevent any diffusion of air into the apparatus, the stem of the funnel on which the filtration was made, dipped

[1] J. Am. Chem. Soc., 19, 223–226. It is evident that Desi misinterpreted the separation of sulphur here, since sulphurous acid alone gives the same result.

[2] This apparatus is similar to that described by H. N. Stokes, Bull. U. S. Geol. Surv. 186.

under water. When an experiment was to be carried out carbon dioxide, which first passed over a long train of red hot copper, was allowed to flow through the apparatus for an hour or more, until the air was removed both from the cylinder and the dropping funnel. The stannous chloride was then quickly decanted from the blue compound, which was then rapidly washed through the dropping funnel by air-free water. The operation requires but a few minutes, during which the substance is wet by the reducing agent. The washing was done at first by air-free water, acidified by hydrochloric acid, and finally by water alone. We, at first, used alcohol and ether to complete the washing, but alcohol absorbs oxygen from the air to a far greater degree than water, and, consequently, had to be discarded. Our earlier preparations were dried in the washing apparatus, or in a vacuum desiccator, which we filled with carbonic acid before exhausting, but despite our utmost pains there were usually signs of oxidation, so that we at last gave up drying entirely and determined the ratio of oxygen absorbed to the tungsten contained in the substance. We insert several analyses of the dried product which were nearly pure, since water is an essential constituent. These were made by heating weighed quantities, noting the losses, and collecting the water. The difference between the total loss and the water found is the quantity of oxygen absorbed from the air.

Table I.—Analyses of Blue Hydroxide (Dry).

	Found.					Aver-age.	Calculated for W_5O_{14}. H_2O.
	I.	II.	III.	IV.	V.		
Time of drying (hours)	14	18	1.5	1.75	1.5	....	....
Weight taken	2.8386	2.8396	3.0575	1.8038	2.7883	....	....
Loss on heat'g	0.0172	0.0188	0.0199	0.0137	0.0173	....	....
P'c'tage loss	0.60	0.66	0.65	0.76	0.62	....	....
Water found	0.0509	0.0514	0.0520	0.0323	0.0452	....	....
P'c't'ge water	1.79	1.81	1.70	1.79	1.62	1.74	1.55
Percentage O absorbed	1.19	1.15	1.05	1.03	1.00	1.08	1.37
O calc. as per cent anhyd. substance	1.21	1.16	1.07	1.05	1.01	1.10	....

The analyses in Table II. were made as follows: As soon
as the tin was completely washed out of the blue compound
the latter was rapidly transferred from the filter into a meas-
ured excess of titrated chromic acid, by means of a wash-bot-
tle filled with air-free water. The mixture was then boiled
for about fifteen minutes, or until complete oxidation was ac·
complished. After cooling, the excess of chromic acid was
titrated by ferrous sulphate in the usual way. The tungstic
acid does not interfere, and the loss of the same by dipping
out is negligible, since a loss of 20 milligrams when
3 grams substance is used, occasions an error of only 0.01
per cent in the oxygen absorbed. After the titration, the
tungstic acid is filtered, washed with dilute hydrochloric acid,
and burned in a platinum crucible to a constant weight. As
soon as the filter is charred, the cover of the crucible is re-
moved. The blast should not be used.

Table II.—Analysis of Blue Hydroxide (Wet).

	I.	II.	III.	IV.	Average.	Calculated for W_5O_{14}.
		Found.				
$K_2Cr_2O_7$ taken (cc.)	50	54.6	50.2	50	....	....
$FeSO_4$ used, in terms of $K_2Cr_2O_7$ (cc.)	29.2	14.8	15.7	16.4	....	....
Available oxygen in $K_2Cr_2O_7$ required in oxidation	0.0209	0.0399	0.0346	0.0336	....	....
WO_3 found	1.5871	3.1092	2.3063	2.7073	....	....
Blue oxide, anhydrous, calculated from $WO_3 - O$	1.5662	3.0693	2.2717	2.6737	....	....
Per cent of oxygen absorbed by blue oxide	1.33	1.30	1.52	1.27	1.35	1.39

Reduction of Tungstic Acid by Hydriodic Acid.

In these experiments the tungstic acid was heated with the
reagent in sealed tubes at about 200° C. About 1.5 grams
WO_3 was used to about 10 cc. of fuming hydriodic acid

(about 1.7 sp. gr.), and the heating was ordinarily continued several hours. We obtained in this way the same indigo-blue substance which we got with stannous chloride, nor did repeated treatment with the reducing agent appear to exercise any influence on the final product. Weak acid did not give a complete reduction, and very concentrated reagent in large excess gave, in one instance, a mixture containing, besides the blue oxide, a black substance which seemed to contain considerable iodide. It was not investigated. All the preparations made with hydriodic acid were analyzed according to the method described on page 331, and a comparison of the results will show that they agree closely with those of Table I.

Table III.—Analysis of Blue Hydroxide Prepared with Hydriodic Acid.

	I.	Found. II.	III.	Average.	Calculated for W_5O_{14}. H_2O.
	Drying in hydrogen, 1–2 hours, at about 60°.	Drying in hydrogen, 1–2 hours, at about 60°.	Drying in hydrogen, about 1 hour, at 100°.		
Portion I.	0.2528	1.1714	1.0550	....	....
Loss on heating	0.0015	0.0083	0.0031	....	....
Percentage loss	0.59	0.71	0.30	....	....
Portion II.	0.7933	1.0432	....	....	....
Water found	0.0135	0.0168	0.0152	....	....
Percentage water	1.70	1.61	1.44	1.58	1.55
Per cent oxygen absorbed	1.11	0.90	1.14	1.05	1.37

Properties of the Blue Hydroxide of Tungsten.

This compound is a deep-blue powder, a little brighter than indigo, and purplish in reflected light. It is insoluble in water containing a little hydrochloric acid, while in pure water it may assume a very fine state of division, apparently forming a colloidal solution as tungstic acid does. The blue hydroxide of molybdenum, recently investigated by Guichard,[1] shows this property to a degree far more marked.

The tungsten compound oxidizes in the air, especially when moist, and if heated changes to tungstic trioxide almost in-

[5] Ann. chim. phys., [7], **23**, 519.

stantly. Bleaching-powder, hydrogen peroxide, permanganic acid, and chromic acid all oxidize it, but not very rapidly in the cold. Hot concentrated sulphuric acid oxidizes it slowly, and concentrated nitric acid rapidly. Concentrated hydrochloric acid has no effect on it. Strong, cold, caustic alkali solutions, if they change it at all, do so very slowly. Heated, they form alkaline tungstate and evolve a gas. 11.5 cc. of this gas was diluted with air and passed over palladium asbestos. The latter glowed brilliantly. The total condensation was 16 cc., which indicated 10.7 cc. hydrogen. Ammonia also reacts with this compound. Ammonium tungstate passes into solution and a very considerable brown residue remains. No gas is evolved. Ammoniacal silver solution is reduced by it.

It is this blue substance which is formed in the well-known test for tungsten by nascent hydrogen. But nascent hydrogen causes a further reduction to WO_2, and finally to the metal, so that it would be more rational to employ a little strong stannous chloride instead. As this test is ordinarily performed, one may overlook 'a very little tungsten, because with tin or zinc and acid the blue color is transitory.

The Bronze Hydroxide of Tungsten.

When the blue hydroxide which has just been described is warmed with concentrated ammonia, a part of the tungsten goes into solution as ammonium tungstate, and there forms, as above stated, a residue which looks brown and only slightly lustrous while covered by the solution, but when washed and dried it appears deep-purple, with a fine bronze luster in reflected light.

Preparation.—The blue oxide, prepared as described previously, is washed quickly into the flask which served in the formation of the blue compound, by a jet of strong ammonia water. The flask is then filled nearly full of ammonia and corked with the Bunsen valve. It should then be gently warmed and put aside to settle. Now the liquid is removed and the treatment repeated. To do this without allowing the

oxide to come in contact with air, let a current of hydrogen slowly force out the liquid through a small syphon, the gas meanwhile replacing the liquid. By a very simple device the same gas current may be made to force in a second portion of ammonia. When 75 cc. of ammonia are used as a portion, the ammonium tungstate may be almost all removed by twice repeating the process. Then fill the flask with boiled water and transfer quickly to the washing apparatus. When the liquid has run through the filter, wash twice with boiled water acidified with sulphuric acid. The analyses of this compound were carried out exactly as described with the blue hydroxide.

Table IV.—Analysis of Bronze Hydroxide (Moist).

	I.	II. Found. III.	IV.	Average.	Calculated for W_3O_8.
$K_2Cr_2O_7$ taken (cc.)	45.3	80.1 79.7	76	....	....
$FeSO_4$ used, in terms of $K_2Cr_2O_7$ (cc.)	39.1	64.8 58.0	56.1	....	....
$K_2Cr_2O_7$ used in oxidation (cc.)	6.2	15.3 21.7	19.9	....	....
Available oxygen in $K_2Cr_2O_7$ used up	0.062	0.0153 0.0217	0.0199	....	....
WO_3 found	0.2593	0.6662 1.0006	0.8263	....	....
Bronze oxide, anhydrous, calculated from WO_3 — O	0.2531	0.6509 0.9789	0.8064	....	....
Per cent of oxygen absorbed by the bronze oxide	2.45	2.35 2.22	2.47	2.37	2.35

The three following preparations were made under conditions similar to those described above. As they were made earlier in point of time, pains were taken to prove that no more tungsten was extracted by ammonia before any acid was added. They were then washed with hydrochloric acid and dried in a vacuum desiccator. The method of analysis was that described on page 331.

Table V.

	I.	Found. II.	III.	Aver-age.	Calculated for W_5O_8. H_2O.	W_4O_{11}. H_2O.	W_2O_5. H_2O.
Time of drying (hours)	1.5	2.5	3.5	....	....	....	....
Weight taken (gram)	0.5440	0.6940	0.6682	....	....	....	....
Loss on heating	0.0068	0.0076	0.0058	....	....	....	....
Percentage loss	1.25	1.09	0.87	....	....	....	....
Water collected	0.0164	0.0202	0.0180	....	....	....	....
Per cent water	3.02	2.91	2.69	2.87	2.57	1.93	3.85
Oxygen abs'b'd	1.77	1.82	1.82	1.80[1]	2.29	1.72	3.42
Oxygen in anhydrous substance (per cent)	1.82	1.87	1.87	1.85	....	....	....

Properties.—In color this compound appears purple, with a fine bronze luster in reflected light. In the dry state it is very beautiful. Its chemical properties are similar to those of the blue hydroxide. It is oxidized by the same reagents, but more readily. It changes first to the blue compound and then to the yellow tungstic acid. It is insoluble in hydrochloric acid, but seems to go into solution somewhat in pure water, like the blue oxide and tungstic acid. Hot caustic alkalies form alkaline tungstate and hydrogen. Desi obtained an anhydrous substance, which analyses indicated to be W_3O_8, by heating ammonium metatungstate, $(NH_4)_2W_4O_{13}$, in closed vessels to a bright redness. He describes it as "a beautiful purple substance with a yellow metallic reflex, insoluble in water, acids, and alkalies."[2]

It is interesting to compare the action of ammonia on the blue oxide, with the results which Desi obtained with those oxides which he prepared by oxidizing metallic tungsten with strong sulphuric acid. All of them, according to him, give metallic tungsten, when treated with strong ammonia. Now, concentrated sulphuric acid oxidizes the blue compound prepared by us to tungstic acid, and it may perhaps be possible

[1] The low results are readily explained by oxidation. It will be noted that the figures are all higher than W_4O_{11} demands, in spite of oxidation.

[2] J. Am. Chem. Soc., **19**, 227.

that Desi's products were mixtures containing unchanged metal.

In addition to the evidence already presented for the two formulas, $W_5O_{14}.H_2O$ and $W_3O_8.H_2O$, we may instance the fact that Guichard, who has recently investigated the blue oxide of molybdenum, prepared and analyzed by methods differing from ours, concludes that the true formula for the same is $Mo_5O_{14}.6H_2O$. The properties of this substance resemble those of $W_5O_{14}.H_2O$. It is, however, completely soluble in pure water, though not in dilute hydrochloric acid, and soluble also in concentrated hydrochloric acid. The result is a green solution, which, according to Guichard, contains $MoCl_4$. Such a green solution is, in fact, obtained when dilute solutions of a molybdate are treated with stannous chloride, while from a tungstate one gets the blue oxide. $W_5O_{14}.H_2O$ differs from $Mo_5O_{14}.6H_2O$ also in its behavior with ammonia, the latter giving MoO_2.

$W_3O_8.H_2O$ finds its analogue among the oxides of uranium. The latter, in its hydrous state, is described as a dark-green powder, but another form appears to exist, closely resembling in appearance the tungsten compound. Berzelius sometimes obtained a purple-brown precipitate, by precipitating with ammonia, a solution of U_3O_8 in acids, and Ebelmen says that when light decomposes uranyl oxalate a hydrated form of U_3O_8 separates in violet-brown flakes.[1]

Very recently, Hallopeau has revised the work on the tungsten bronzes.[2] There are two series of these interesting compounds. The first is prepared by reducing the tungstates at a red heat in dry hydrogen. They possess the general formula $W_3O_8.M_2O$, where M = Na or K. These bodies possess a metallic luster, and the potassium compound is described as a violet-red substance with a copper reflex, recalling $W_3O_8.H_2O$ in a striking way. The members of the second series (with exception of the barium compound) are made by reducing the molten tungstates with metallic tin. They possess the general formula $W_3O_{14}.M_2O$, where M = Na, K, Li, or

[1] Gmelin-Kraut : Handbuch der Chemie, 2.2, 382.
[2] Ann. chim. phys., [7], **19**, 106 (1900).

22–27

½Ba, and are all dark-blue in color like $W_5O_{14}.H_2O$. So far as composition goes, then, the two compounds described in this paper are the mother-substances of the tungsten bronzes, though it remains to be proved that the connection can be experimentally made.

Assuming our formulas to be correct, the reduction of tungstic trioxide by stannous chloride and hydrochloric acid, or by hydriodic acid, consists in the addition of hydrogen :

$$5WO_3 + 2H = W_5O_{15}H_2.$$
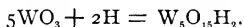
The study of colloidal tungstic acid indicates a molecule much more complex than WO_3, and other facts are in harmony with this. It is easy to represent such a molecule by a ring structure according with the valence hypothesis, and ring structures usually go with chemical stability. Tungstic acid at any rate shows a much greater stability than its chromium and molybdenum analogues, and it is not impossible that in the above reduction a single complex molecule is reduced like many organic compounds where oxygen becomes hydroxyl. The action of ammonia on $W_5O_{15}H_2$ may be represented thus :

$$W_5O_{15}H_2 + 4NH_4OH = 2(NH_4)_2WO_4 + W_3O_9H_2 + 2H_2O.$$

The Action of Hydroxylamine on a Soluble Tungstate.

When hydroxylamine hydrochloride is introduced into a solution of sodium tungstate a white precipitate is obtained, which is faint yellow on drying. It does not appear to be crystalline. In water it is moderately soluble, so that the washing which is necessary in its preparation is quite wasteful. Our preparations were washed with very cold water till chlorine was removed, then with alcohol and ether, and dried in the air. The compound decomposes rather violently, but without detonation, when it is heated. The analyses agree closely with the formula

$$4NH_2OH.3WO_3.3H_2O,$$
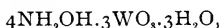
indicating simply a hydroxylamine tungstate. There appears to be no other tungstate of this type, the ammonium salt, $4(NH_4)_2O.3WO_3.3H_2O$, mentioned by Gmelin-Kraut, really possessing another formula.[1]

[1] Gmelin-Kraut: Handbuch der Chemie, 2,.2, 115 ; see Ann. chim. phys., [3], **69**, 23.

I. 0.2375 gram substance gave 0.1869 gram WO_3.

II. 0.2621 gram substance gave 0.2046 gram WO_3.

III. 0.8603 gram substance gave 47.8 cc. moist N at 16° C. and 714.2 mm.

IV. 1.3079 gram substance gave 74.5 cc. moist N at 20° C. and 717.5 mm.

0.9880 gram substance gave, on combustion, 0.1795 gram H_2O.

1.1054 grams substance lost, at 100° C., 0.0669 gram.

V. 1.3298 gram substance gave 1.0575 gram WO_3.

1.0009 gram substance gave, on combustion, 0.1816 gram H_2O.

1.0343 gram substance gave 57.6 cc. moist N at 25.8° C. and 720.5 mm.

Table VI.

	I.	II.	Found. III.	IV.	V.	Average.	Calculated for $4NH_2OH$. $3WO_3.3H_2O$.
Nitrogen	....	....	6.18	6.28	6.05	6.17	6.33
Total water[1]	....	....	....	(18.17)	(18.15)	(18.16)	(18.32)
Water of crystallization	....	....	....	6.05	....	6.05	6.11
H in excess of that in the crystal water	....	....	....	1.35	1.35	1.35	1.35
WO_3	78.70	78.05	....	....	79.52	78.75	78.96
O in excess (by diff.)	....	....	....	....	....	7.69	7.24

Summary.

1. WO_3 is reduced with greater difficulty than MoO_3 and CrO_3. In alkaline solution it is not reduced by grape sugar, hydroxylamine, or metallic aluminium. Hydroxylamine simply forms a sparingly soluble tungstate. Hydrochloric acid, with either oxalic acid or alcohol, is without reducing action, and the same is true of sulphurous acid in sealed tubes.

2. Fuming hydriodic acid or stannous chloride solution re-

[1] Obtained by combustion with copper oxide.

duces tungstic acid to an insoluble indigo-blue hydroxide, $W_5O_{14}.H_2O$. It is readily oxidized by the air and oxidizing agents, and dissolves in hot caustic alkalies with evolution of hydrogen. It finds an analogue in the blue hydroxide of molybdenum, $Mo_5O_{14}.6H_2O$, and may be considered as the mother-substance of one of the series of tungsten bronzes having the general formula $W_5O_{14}.M_2O$. It is this compound which is formed by nascent hydrogen in the well-known test for tungsten.

3. When the above compound is acted upon by strong ammonia water, a part of the tungsten dissolves out as ammonium tungstate, and there remains a brown residue which dries to a beautiful purple powder with a decided bronze luster. Its formula is $W_3O_8.H_2O$. Its chemical properties are similar to those of the blue compound. Among the oxides of uranium we find the analogous $U_3O_8.xH_2O$, and the series of tungsten bronzes of the general formula, $W_3O_x.M_2O$, may be looked upon as its derivatives.

This work is published in an unfinished condition because the authors were obliged to separate. It is the intention of one of us to carry on further studies in this field.

MISSOURI STATE SCHOOL
OF MINES.

A CHEMICAL METHOD FOR OBTAINING VACUA.

BY FRANCIS G. BENEDICT AND CHARLOTTE R. MANNING.

The production of a "good" vacuum, especially in desiccating apparatus, is frequently required in the chemical laboratory. Mechanical air pumps, so successfully used in the exhaustion of incandescent light bulbs, are obviously impracticable for ordinary laboratory use, and the valve pump of the physical lecture table is, in general, the most available form of pump for producing a vacuum. In the chemical laboratory one has, as a rule, to be content with the vacuum obtained by means of one of the many forms of water pumps unless, as is occasionally the case, a mercury pump is at hand. The length of time required to exhaust a vessel by means of the mercury pump is considered so great an objection to its

every day use that the apparatus is commonly allowed to become dirty and ultimately inoperative, awaiting a special and pressing need before being put in working order.

Though water pumps are almost universally adopted as the most practicable instrument for producing vacua in the laboratory, their use is attended with numerous difficulties, chief of which is the irregularity in water pressure, resulting in a too frequent "sucking back" of water, especially towards the end of an exhaustion. Where great inequalities in water pressure are common, it is customary to insert an empty bottle between the pump and the vessel to be exhausted to collect any water that may inadvertently be sucked back. This bottle, while serving its original purpose, obviously increases the volume of air to be removed, and consequently the time required to complete the operation.

With constant and high water pressure and otherwise ideal conditions, few, if any, forms of water pump will give a vacuum corresponding to a mercury pressure of less than 10 mm.

It is more frequently the case, however, that the water pump available at any particular time falls far short of this efficiency, and, indeed, by being so inferior, materially delays the drying operation that is dependent on a good vacuum.

So far as we are aware, the use of chemical means for obtaining vacua has never been generally adopted. The absorption of a gas or vapor filling a space by means of some suitable non-volatile absorbent is, however, capable of yielding vacua of the highest degree of perfection.

Regnault,[1] in some of his experiments on hygrometry, made use of the absorbing action of concentrated sulphuric acid towards aqueous vapor to produce a vacuum. He exhausted a large glass globe in which a few grams of water had been placed until all the water had vaporized, thereby expelling the air. By shaking the globe, he was able to break a small glass bulb which had previously been filled with concentrated sulphuric acid, hermetically sealed and inserted in the large globe. The concentrated acid rapidly absorbed the water vapor, thereby producing a very perfect vacuum.

[1] Ann. chim. phys., [3], **15**, 190 (1845).

The absorption by potassium hydroxide of residual carbon dioxide in a vessel previously filled with the gas, and then partially exhausted, was first used by Andrews.[1]

Brunner[2] substituted calcium hydroxide for potassium hydroxide, and made use of the fact that dry calcium oxide will not absorb dry carbon dioxide in establishing the conditions under which the operation is best conducted. At the end of the preliminary exhaustion by the water pump or air pump, the calcium oxide is moistened with a small quantity of water. The carbon dioxide is absorbed, the aqueous vapor resulting being finally absorbed by concentrated sulphuric acid in a dish at the bottom of the vessel to be exhausted. In two hours a nearly perfect vacuum was thereby obtained in a half-liter vessel of special construction.

He further suggests the use of ammonia in the place of carbon dioxide, absorbing the gas by concentrated sulphuric acid.

Newth[3] has adopted this suggestion in a very striking lecture experiment, though the practicability of this method as a laboratory agent is very doubtful.

Pflüger[4] demonstrated very clearly the agency of water vapor in removing air from a vessel during the process of exhaustion. In an apparatus of special construction he vaporized water by exhausting the air by means of a water pump. On introducing concentrated sulphuric acid he was able to lower the tension of the residual gas to 1 or 2 mm. of mercury. He suggests the introduction of concentrated sulphuric acid into vacuum desiccators after, and not before, exhaustion, though no description of a practical apparatus involving the use of this principle is included in his article.

Other applications of chemical reactions in obtaining vacua with special reference to perfecting the Torricellian vacuum include those of Gassiot,[5] who used metallic sodium in a rarefied atmosphere of pure oxygen, and applied Andrews'[6] method

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[1] Phil. Mag., 1852, p. 104 ; Ann. Phys. und Chem., 88, 309 (1853).

[2] Ann. Phys. und Chem., 94, 523 (1855).

[3] "Chemical Lecture Experiments," London, 1892, p. 58.

[4] Archiv. f. die Ges. Physiologie, 38, 311 (1886).

[5] Phil. Trans., 149, 147 (1859).

[6] *Loc. cit.*

to the preparation of vacuum tubes,[1] and Crookes,[2] who used sulphur to absorb mercury vapor and copper to absorb any traces of sulphur vapor.

While not, strictly speaking, the result of chemical agency, the absorption of the residual gas by charcoal, as suggested by Dewar and Tait,[3] the freezing of the mercury vapor in a Torricellian vacuum by liquid air,[4] and the freezing of air by liquid hydrogen,[5] as shown by Dewar, should be mentioned.

In determining the amount of water in organic compounds, especially those of a physiological nature, the greatest precaution is necessary to prevent overheating and consequent partial disintegration of the complex molecule, and, on the other hand, it is a well-known fact that many bodies of an organic nature persistently retain moisture, necessitating prolonged drying *in vacuo*. In such instances, the more perfect the vacuum the more rapid and complete the drying.

When the effect of a vacuum is accompanied by the use of a powerful dehydrating material, to absorb the water vapor constantly arising from the material undergoing desiccation, the conditions for rapid and complete drying are ideal.

Cooke and Richards[6] pointed out the necessity of placing the drying agent in the upper portion of the space to be dried.

Hempel[7] gave a striking experiment to show quantitatively the advisability of this disposition of the drying agent, and devised his admirable and well-known vacuum desiccator,[8] which is constructed on this principle. In all our work this form of desiccator has been used.

A small mercury manometer was placed inside the desiccator to indicate the degree of exhaustion. With the water pump at our disposal, the air could only be rarefied to a pressure of about 40 mm. The large size of the apparatus precluded the use of a mercury pump for rapid work, and a

1 Proc. Roy. Soc., **10,** 244 (1860).
2 Phil. Trans., **159,** 300 (1878).
3 Proc. Roy. Soc., Edinburgh, 8, 348 (1875).
4 Proc. Roy. Inst., **14,** 1.
5 Proc. Roy. Soc., **64,** 231 (1898).
6 Proc. Am. Acad., **23,** 159 (1887).
7 Ber. d. chem. Ges., **23,** 3566 (1890).
8 Ztschr. angew. Chem., 1891, p. 201.

chemical means for securing the desired diminution in pressure was ultimately used.

We have found that, after expelling the air in the desiccator with ether vapor, the residual vapor is entirely absorbed by the sulphuric acid in the upper chamber, yielding a remarkably good vacuum.

The exact conditions under which the operation is best conducted are as follows :

Fresh, concentrated sulphuric acid (about 150 cc.) is placed in the previously cleaned and dried upper compartment of the desiccator.   After introducing the material to be dried (in appropriate containers), and just before the cover is put in place, 10 cc. of pure anhydrous ether are delivered from a pipette upon the bottom of the desiccator in such a manner as not to come in contact with the material to be dried.   The cover is then carefully put on, the glass stop-cock being left open.   Immediately the water pump is connected with the tube in the cover and the exhaustion continued until the manometer shows from 40 to 60 mm. pressure.   The stop-cock is then closed, the tube connecting with the water pump removed, and the desiccator allowed to stand.   In a very few minutes a vacuum of from 4 to 1 (or even less) mm. is obtained.   With the desiccators in use in this laboratory, this degree of exhaustion is obtained in from eight to twelve minutes after putting the cover on the desiccator.

After the water pump has been disconnected, the absorption of the ether vapor may be considerably accelerated by so rotating the desiccator held in the hands as to agitate the acid and moisten a larger surface of glass in the top compartment. Obviously this procedure can only be carried out with due care for the stability of the dishes in the desiccator.

In the size of apparatus used in our experiments the lower compartment, representing the efficient space for desiccating, contains 2100 cc. ; this, together with the 1400 cc. of space in the upper compartment when containing 150 cc. of acid, gives a total gas volume of 3.5 liters to be exhausted.

Obviously a desiccator of the Hempel type is especially advantageous for use in connection with this method for obtain-

ing vacua, as the ether vapor completely fills the lower compartment, expelling the lighter air before the sulphuric acid in the upper compartment effects any great absorption of the ether vapor. Indeed it is doubtful if the method can be used with anything like this degree of efficiency with desiccators of any other type. We have found these desiccators to be remarkably tight, vacua of about 1 mm. pressure being unchanged at the end of two weeks.

We have no data as to how many charges of ether 150 cc. of sulphuric acid will absorb, but the same acid has been used in the operation of exhausting the desiccator three times with no noticeable diminution in the efficiency of absorption.

This method is especially adapted for use in the chemical laboratory, for (1) the apparatus required is that already in use in many laboratories, (2) the time requirement to secure a good vacuum is reduced to a minimum, and (3) no ordinary method will permit of so complete a rarefication of the gases in the desiccator.

The application of this method in obtaining high vacua other than in desiccators has more to do with the physicist than the chemist, the only object of this paper being to present to the chemical laboratory a simple and rapid means for obtaining a good vacuum.

MIDDLETOWN, CONN.

XCVI.—ON THE MIXED CRYSTALS OF SILVER CHLORATE AND SODIUM CHLORATE, AND THEIR SOLUTIONS.

BY H. W. FOOTE.

I.

In a previous article[1] it has been shown that when two salts crystallize from aqueous solution, depositing mixed crystals of two crystalline forms, the composition of the crystals at the mixing limit should, in general, change with the change of temperature. Experiments to prove this were carried out

[1] This JOURNAL, **26**, 418 (1901).

with mixed crystals of copper and zinc sulphates. In the present investigation one of the objects has been to show that the composition of mixed crystals of silver chlorate and sodium chlorate at the mixing limit changes with change of temperature.

Retgers has shown[1] that silver chlorate and sodium chlorate form mixed crystals very readily. He found that sodium chlorate crystallizes in cubes containing up to 11 molecular per cent of silver chlorate, while silver chlorate crystallizes in the tetragonal system, containing as much as 41.75 molecular per cent of sodium chlorate. The temperature of the experiments was the ordinary room temperature. As will be shown later, these values are slightly below the real mixing limits for that temperature.

In the experiments to be described, pure sodium chlorate and silver chlorate were required. The former was prepared by recrystallizing the commercial product, which contained a small amount of chloride. Barium chlorate was the starting point for silver chlorate. To a solution containing a known amount of the barium salt, a calculated quantity of sulphuric acid was added, just sufficient to precipitate all the barium as sulphate. The precipitate was removed by filtration, and the filtrate, containing practically pure chloric acid in solution, was saturated with silver carbonate, prepared by precipitating silver nitrate with sodium carbonate. The solution of silver chlorate was filtered from the excess of silver carbonate, evaporated, and silver chlorate obtained by crystallization. The product was purified by repeated crystallization. It was found, on analysis, to be pure.

In determining the mixing limits of the two forms, solutions were used having a volume of 300 to 400 cc. A small quantity of crystals forming from this volume of solution would alter the composition of the mother-liquor but very slightly. The relative proportions of the two salts in solution were varied until both cubes and tetragonal crystals formed at the same time in approximately equal amount. The two forms of crystals were so unlike that they could be distinguished at a

[1] Ztschr. phys. Chem., **5,** 438 (1890).

glance and separated mechanically. It was usually found best to add a minute quantity of the two salts to start the crystallization, and those crops only were analyzed in which both forms could be obtained pure.

Silver chlorate was determined in the crystals by titration with ammonium thiocyanate, and sodium chlorate by difference. The solutions were analyzed by evaporating weighed quantities to dryness and heating in an air-bath at about 120°. The residue, after weighing, was dissolved in water and titrated with thiocyanate solution, to obtain the amount of silver chlorate present. Sodium chlorate was then calculated by difference.

The experiments were carried out at 12°, 25°, 35°, and 50°. An Ostwald thermostat was used for the three higher temperatures, while for 12° a thermostat which I have previously described[1] was used. The latter ran constantly for a month or more with practically no attention and maintained a very even temperature.

In tabulating the results (Table I.) the mixing limits of the two forms of crystals are given in the first and second columns. The number of molecules of sodium chlorate and of silver chlorate to 100 molecules of water are given in the third and fourth columns, respectively, representing the composition of the solutions from which the two forms of crystals were obtained, while in the fifth column is given the molecular percentage of sodium chlorate in the total amount of dissolved silver and sodium chlorates in the solutions. The four analyses for each temperature were made from separate crops of crystals. The following results were obtained :

Table I.—Mixing Limits of Cubes and Tetragonal Crystals of Sodium and Silver Chlorates.

Tetragonal. Molecular per cent of $NaClO_3$.	Cubes. Molecular per cent of $NaClO_3$.	Mols. $NaClO_3$: 100 mols. H_2O.	Mols. $AgClO_3$: 100 mols H_2O.	Molecular per cent $NaClO_3$ in dissolved chlorates.
		$T = 12°$.		
49.13	85.54	13.85	0.249	98.23
50.45	84.41	13.87	0.301	97.87
50.85	85.48	14.01	0.289	97.98
49.71	87.26	14.14	0.291	97.98

[1] Ztschr. phys. Chem., **33**, 749 (1900).

Tetragoual. Molecular per cent of NaClO₃.	Cubes. Molecular per cent of NaClO₃.	Mols. NaClO₃ : 100 mols. H₂O.	Mols. AgClO₃ : 100 mols H₂O.	Molecular per cent NaClO₃ in dissolved chlorates.
		$T = 25°$.		
48.27	81.12	15.35	0.418	97.35
48.61	81.63	....	....	....
48.08	83.52	....	....	....
47.80	79.94	15.59	0.481	97.01
		$T = 35°$.		
48.65	81.02	17.28	0.568	96.81
47.45	79.03	17.26	0.737	95.91
47.84	76.61	16.66	0.596	96.55
47.73	76.43	16.87	0.645	96.32
		$T = 50°$.		
47.27	74.08	19.34	1.019	95.00
47.78	75.96	19.42	0.966	95.26
47.13	74.77	19.35	0.980	95.18
46.20	68.93	....	....	....

The results, especially those for the cubes, vary considerably among themselves, as a very slight change in the composition of the solutions produces a very large change in the mixed crystals. The average values for each temperature are given in Table II., and it is believed that these represent very nearly the true mixing limits.

Table II.—Averages Computed from Table I.

Temp.	Tetragoual. Molecular per cent of NaClO₃.	Cubes. Molecular per cent of NaClO₃.	Mols. NaClO₃: 100 mols. H₂O.	Mols.AgClO₃: 100 mols. H₂O.	Molecular per cent NaClO₃ in dissolved chlorates.
12°	50.04	85.67	13.97	0.283	98.02
25°	48.19	81.55	15.47	0.450	97.18
35°	47.92	78.27	17.02	0.636	96.40
50°	47.10	73.44	19.37	0.988	95.15

The results in Table II. are shown graphically in Fig. I., where the temperatures are plotted as ordinates and the molecular percentages of sodium chlorate at the mixing limit as abscissas. It is quite evident that the mixing limit varies with the temperature, though in the case of the tetragonal crystals the change is very slight. The curve AB, representing the varying composition of the cubes at the mixing limit, is a straight line. If continued downward, it would inter-
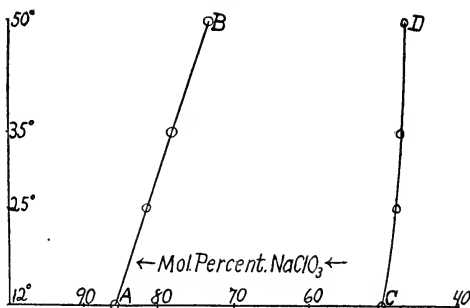
Fig. I.

sect the temperature axis at about —30°, that is, at —30°
sodium chlorate in cubes should be unable to form mixed
crystals with silver chlorate. This would make it appear very
probable that the crystalline form of sodium chlorate changes
at this temperature. The curve *CD* shows that as the tem-
perature is lowered tetragonal silver chlorate can take up in-
creasing amounts of sodium chlorate. It thus seems most
probable that sodium chlorate would assume the tetragonal
form below —30°, and be completely isomorphous with silver
chlorate. If this interpretation of the results be correct, it in-
dicates a method of determining the transition temperature
of a salt by means of its mixed crystals.

II.

A second object of this investigation has been to determine
the relations existing between the salts in solution and the
mixed crystals. In what follows, I shall use the following
symbols : y represents the molecular percentage of the more
soluble salt, as sodium chlorate, in the total amount of dis-
solved salts, and x the molecular percentage of that salt in
the mixed crystals. Roozeboom has shown[1] that when mixed
crystals form in two different crystalline modifications, as is
the case with sodium and silver chlorates, the solutions from
which the two forms are deposited are of two classes as re-
gards the mixed crystals :

[1] Ztschr. phys. Chem., 8, 504 (1891).

I. The value of y, when the solution deposits both forms of crystals, lies between the values of x for the two forms at the mixing limit (Case IV. of Roozeboom).

II. The value of y is greater than either of the values of x at the mixing limit (Case V. of Roozeboom).

Roozeboom investigated[1] solutions of potassium and thallium chlorates, and the mixed crystals formed from them, and found they belonged to Class I., as is evident from the following values :

$$y = 93.25, \qquad\qquad x = 36.30 \text{ and } 97.93.$$

In this case y represents the percentage of potassium chlorate in the dissolved chlorates, and x the percentage of potassium chlorate in the two crystallized forms at the mixing limits. It will be noticed that y lies between the two values of x. Similar results have been obtained by Muthmann and Kuntze[2] with the permanganates of potassium and rubidium, and by Fock[3] with the following pairs of salts : Potassium and ammonium chlorides, potassium and ammonium bromides, potassium and thallium nitrates, and copper and nickel sulphates. In this class, solutions depositing crystals of one form only, when concentrated, change their proportions of salts till they reach a concentration where both forms of mixed crystals are deposited together. On further evaporation the composition of the solution remains fixed and both forms crystallize together as long as any solution remains. It will be noticed, by reference to Table II., that the value of y, representing the molecular percentage of sodium chlorate in the solutions, is greater than either value of x, the molecular percentage of sodium chlorate in the mixed crystals. Evidently this example belongs under Class II., though Roozeboom[4] was inclined to believe, from the work of Retgers, that the salts belonged in the first class, behaving like thallium and potassium chlorates. I believe only one example of this class has previously been described, that of the mixed double chlorides of copper with ammonium and potassium by

1 Ztschr. phys. Chem., 8, 531 (1891).

2 Ztschr. f. Kryst., 23, 368.

3 *Ibid.*, 28, 337.

4 Ztschr. phys. Chem., 8, 528 (1891).

Fock.[1] In this class, when a solution is concentrated, the proportion of the more soluble salt will increase in the solution as water is removed, till the solution is completely evaporated.

It seemed desirable to show (1) whether the relation $y>x$ holds true for the chlorates at all points where the concentration of the solution is such that only one form of crystal is deposited, and (2) what is the influence of temperature on the relative values of y and x. Solutions containing different proportions of silver and sodium chlorates were accordingly prepared in such concentrations that a small amount of mixed crystals separated at the temperature desired. The volume of the solutions was, as before, 300 to 400 cc. The experiments were carried out in the thermostat as before.

The following results were obtained (Table III). The values at the mixing limits are taken from Table II.

Table III.

Tetragonal. Molecular per cent of NaClO₃. x_1.	Cubes. Molecular per cent of NaClO₃. x_2.	Mols. NaClO₃. 100 mols. H₂O.	Mols. AgClO₃. 100 mols. H₂O.	Molecular per cent of NaClO₃ in dissolved chlorates. y.
		$T = 12°$.		
....	94.45	14.73	0.111	99.23
....	92.76	14.39	0.165	98.87
....	90.15	14.30	0.197	98.64
50.04	85.67	13.97	0.283	98.02
42.05	....	9.22	0.360	96.24
32.12	....	6.89	0.478	93.52
13.11	....	3.61	0.550	86.77
5.04	....	1.46	0.695	67.79
		$T = 25°$.		
....	93.65	16.93	0.232	98.65
....	85.06	16.14	0.385	97.67
48.19	81.55	15.47	0.450	97.18
31.97	....	8.37	0.742	91.85
25.74	....	7.34	0.798	90.19
9.71	....	3.62	1.03	77.77
4.00	....	2.37	1.14	67.46
3.04	....	1.72	1.17	59.55

[1] Ztschr. phys. Chem., **12**, 657 (1893).

Tetragonal. Molecular per cent of NaClO$_3$. x_1.	Cubes. Molecular per cent of NaClO$_3$. x_2.	Mols. NaClO$_3$: 100 mols. H$_2$O.	Mols. AgClO$_3$: 100 mols. H$_2$O.	Molecular per cent of NaClO$_3$ in dissolved chlorates. y.
		T = 35°.		
....	98.00	19.14	0.090	99.53
....	95.20	18.60	0.196	98.94
....	91.72	18.12	0.310	98.29
....	89.77	17.91	0.338	98.15
....	88.24	17.83	0.431	97.64
47.92	78.27	17.02	0.636	96.40
46.81	....	16.02	0.637	96.17
42.11	....	12.82	0.804	94.10
37.20	....	11.20	0.941	92.25
23.09	....	7.59	1.16	86.76
12.06	....	4.69	1.38	77.25
5.86	....	3.31	1.49	68.98
3.66	....	2.33	1.65	58.49
		T = 50°.		
....	94.27	21.15	0.289	98.65
....	79.86	19.59	0.875	95.73
47.10	73.44	19.37	0.988	95.15
42.69	....	16.02	1.25	92.76
34.87	....	12.67	1.54	89.18
17.71	....	7.80	2.08	78.97
6.60	....	4.06	2.37	63.09
3.38	....	1.98	2.85	41.04

It will be noticed that for all temperatures the values of y are greater than the corresponding values of x, that is, the proportion of sodium chlorate in the solutions is always greater than in the mixed crystals which are deposited from them.

In Fig. II., the values of x and y taken from Table III. are plotted as abscissas and ordinates, respectively, for the temperatures 25° and 50°. From the diagram it is evident that as the temperature rises the values of x and y become more nearly equal, that is, the composition of the mixed crystals will approximate more nearly to the composition of the solutions from which they form.

The following conclusions may be drawn from the results as regards obtaining the pure salts from the mixed crystals by recrystallization : Silver chlorate could be obtained prac-
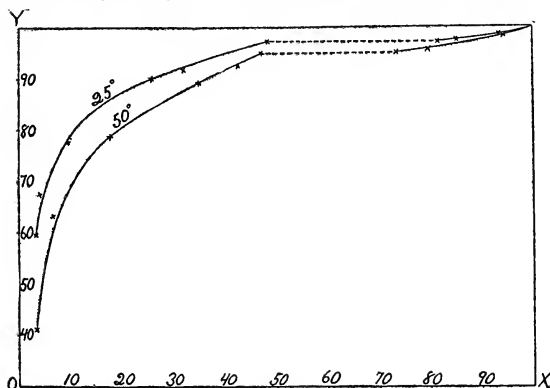
Fig. II.

tically pure by recrystallizing, as the proportion of it in the crystals is always greater than in the solution. On the other hand, to obtain pure sodium chlorate by recrystallizing the mixed crystals would be impossible, even though the mixed crystals at first were nearly pure sodium chlorate. The recrystallized product would always contain more silver chlorate than the mother-liquor. In this case a purer product would be obtained by evaporating the mother-liquor than from the recrystallized product. Silver chlorate could be obtained more readily in a pure condition if the recrystallization were carried on at a low temperature, for the proportion of silver chlorate in the mixed crystals deposited from a given solution is greater, the lower the temperature.

Summary.

1. The composition of mixed crystals of sodium and silver chlorates at the mixing limit changes with a change in temperature.

2. The percentage of sodium chlorate in the total amount of dissolved chlorates in a solution is greater than in the mixed crystals from the solution.

3. As the temperature is raised the percentage of sodium chlorate in the total amount of dissolved chlorates becomes

more nearly equal to the percentage of this chlorate in the mixed crystals.

4. Silver chlorate may be obtained pure by recrystallizing the mixed chlorates.

5. Sodium chlorate cannot be obtained pure by recrystallizing the mixed chlorates, for the recrystallized product contains more silver chlorate than the mother-liquor.

THE ELECTROMOTIVE FORCE OF METALS IN SOLUTIONS OF CYANIDE.[1]

By S. B. CHRISTY.

In reviewing my paper '' On the Solution and Precipitation of Cyanide of Gold,''[2] Mr. E. B. Wilson contends[3] that '' in the solution of gold by means of alkaline cyanides the various reactions are determined as to their order and intensity by the relative positions of the elements concerned in the electrochemical series, or series of voltaic tension.''

In a modified form this statement is probably true. That is to say, the difference of electrical potential in any closed electrical circuit determines the nature of the reactions which ensue. But the matter is not so simple as Mr. Wilson assumes. Recent investigations show that the order of the metals in the electrochemical series depends not only on the nature of the elements themselves, but also on the chemical composition of the solution in which they are placed, its degree of concentration, its temperature, and, in the case of gases, on the pressure.

Unless all these conditions are taken into account, inferences drawn from the electrochemical series are likely to prove more misleading than useful. The series, as quoted by Mr. Wilson from Gore, is as follows :

3	Potassium	28	Antimony
4	Sodium	29	Tellurium
8	Calcium	31	Gold
9	Magnesium	37	Carbon

[1] Communicated by the author and based upon an article in the Transactions of the American Institute of Mining Engineers, Vol. 30.

[2] Trans. Am. Inst. Min. Eng., **26**, 735.

[3] *Ibid.*, **27**, 821.

12	Manganese	39	Nitrogen
13	Zinc	40	Arsenic
15	Iron	43	Sulphur
20	Lead	45	Bromine
24	Copper	46	Chlorine
25	Hydrogen	47	Oxygen
27	Silver		

This series correctly shows the difference of potential in many solvents, especially in acid solutions, but the use of it for predicting the action of cyanide solutions involves several grave errors, one of which is the assumption that the nature of the solution in which substances are placed is without effect on the order of the series.

The remarkable effect of solutions of cyanide of potassium upon the relative positions of substances in the electrochemical series was first shown by Prof. Jacoby, who, on August 21, 1844, called the attention of the St. Petersburg Academy of Sciences to the fact that when silver and cyanide of potassium solution replace the zinc and sulphuric acid in the Daniell cell, a strong current ensues and copper is precipitated. Ordinarily, and according to the usual inference from the above series, copper precipitates silver from its solutions, but here was a combination in which silver precipitated copper.

In the following year, Poggendorff announced[1] that by his (now well-known) "compensation method," he had found the electrochemical series in 1 part of potassium cyanide to 8 parts water—*i. e.*, in a 12.5 per cent solution of potassium cyanide, to be :

1	Zinc amalgamated	9	Lead
2	Zinc	10	Mercury
3	Copper	11	Palladium
4	Cadmium	12	Bismuth
5	Tin	13	Iron
6	Silver	14	Platinum
7	Nickel	15	Cast-iron
8	Antimony	16	Carbon

Gore[2] also investigated this subject with similar results, only

[1] Pogg. Ann., **66**, 597 (1845).
[2] Proc. Roy. Soc. (London), **30**, 45 (1879).

he showed that the order depends on concentration and temperature, and that, according to these conditions, gold may be more or less electro-positive than silver.

The variations thus discovered in the relative position of the metals in the electrochemical series at once cast a cloud on its usefulness for predicting chemical reactions; and though a great mass of experimental data was accumulated, and the most acute minds of the century were brought to bear on the problem, no explanation of these anomalies was found for many years.

It is only within the last decade that anything like a clue to the mystery has been detected; and this result has been made possible only through the combined efforts of a number of men who approached the subject from what may be almost termed its purely speculative side, without any thought of practical applications.

Methods Used in This Investigation.

In looking about for some means of determining the relative affinities of the metals for cyanide solutions, I long ago came to the conclusion that the determination of the relative electromotive forces of the metals in solutions of different strengths was the simplest, readiest, and most certain that could be selected. For, properly considered, it shows the actual tendency of the metal to go into solution. My first experiments were made in this direction in August, 1896. I made at that time a large number of preliminary determinations, the results of which were presented in a lecture given February 1, 1897, before the California Academy of Sciences, in San Francisco.

The results of these experiments have filled me with constant surprise, when I have noticed what apparently slight causes were capable of making great changes in the electromotive force of the same metal. The great delicacy of the method proved to be the chief source of difficulty in its application, while at the same time it reported faithfully the facts as they exist in nature.

Two methods have been used in these determinations, the first being what I have, for brevity, called the "Deflection"

method, and the other the "Compensation" or "Zero" method of Poggendorf.

In each case an electrolytic cell is constructed with two electrodes, each immersed in a separate solution. One, consisting of the metal to be tested, was held in the points of a platinum-tipped pair of forceps, electrically connected with a galvanometer, and was immersed in a vessel containing the cyanide solution of the given strength. The other was in all cases the "normal" electrode of Prof. Ostwald, consisting of mercury, electrically connected with the galvanometer by means of a glass-coated platinum wire. The surface of the mercury is covered with a layer of mercurous chloride, a couple of inches thick, and a solution of chloride of potassium of 1 gram-molecule $\dfrac{M}{1}$ (in this case also a normal solution).

The purpose of the normal electrode of Ostwald is to have a non-polarizable electrode in a solution of known strength and electromotive force. This is fixed at —0.560 volt. That is, in the case of the normal electrode, the mercury ions tend to precipitate themselves on the surface of the mercury, and the solution is therefore negative to the metal by 0.560 volt. That is, the positive current tends to flow through the solution to the mercury, which becomes positively electrified, while the solution itself becomes negatively electrified.

If we neglect the slight electromotive force due to the contact of the two solutions, the resulting electromotive force of the combined cell is the algebraic sum of the electromotive forces active at the two electrodes. Hence, if we subtract 0.560 from the electromotive force of the cell, we have the electromotive force of the metal under consideration. The algebraic sign indicates the direction of the positive current.

The Deflection Method.—This method is much the most convenient for such investigations, particularly in the first roughing out of a large amount of material. With proper precautions it gives results not less reliable than those obtained by the zero method, and it has the great advantage over the latter that the rapid changes of electromotive force may be followed almost as they occur.

The method is illustrated in Fig. I. B is the cell containing the cyanide solution and the metal M to be tested, NE is Ostwald's normal electrode, R is a resistance which varied in the tests from 30,000 to 200,000 ohms, G is a Wiedemann reflecting galvanometer, K, a make-and-break circuit key, and C a commutator.

THE DEFLECTION - METHOD.
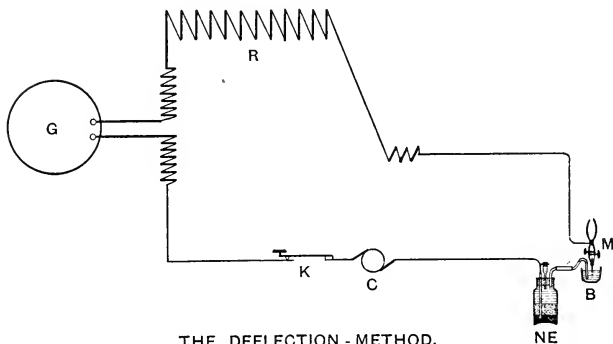
B,	Cell Containing Cyanide Solution;	R,	Resistance of from 30,000 to 200,000 Ohms;
M,	Metal to be Tested;	G,	Wiedemann's Reflecting Galvanometer;
NE,	Ostwald's Normal Electrode;	K,	Make - and Break - Circuit Key.

Fig. I.

The galvanometer was calibrated by replacing the cells B and NE with a Clark cell, prepared according to the directions of Ostwald, and noting the deflection produced by its voltage through the given resistance of 30,000 to 200,000 ohms. The voltage was taken as electromotive force $= 1.438 -$ 0.001 $(t^0 - 15°$ C.) volts.

Most of the concentrations of potassium cyanide were $\dfrac{M}{I}$ (one gram-molecule, 65 grams per liter, or 6.5 per cent), or fractional multiples of this in tenths. Thus the series used was frequently $\dfrac{M}{I}$, $\dfrac{M}{10}$, $\dfrac{M}{100}$, $\dfrac{M}{1,000}$, $\dfrac{M}{10,000}$, $\dfrac{M}{100,000}$, $\dfrac{M}{1,000,000}$.

As there is no little difference in the methods of notation in use, and much resulting confusion, the following methods of notation will always be used in this paper : We shall follow the motion of the positive ions through the solution, and the mode of notation will depend entirely on that. When the motion of the positive ion in the solution is from the metal to the solution, the metal is said to be electropositive, because it gives up positive ions to the solution and causes the solution to become positively electrified, itself becoming at the same time negatively electrified. Such, for instance, is the case of zinc in a solution of zinc sulphate. When, on the other hand, the solution gives up positive ions to the metal immersed in it, as is the case with copper in a solution of copper sulphate, the metal is said to be electronegative, for it causes the solution in which it is immersed to become electronegative, itself, at the same time, becoming positively electrified. The mercury in Ostwald's normal electrode is another example. The + or − sign, then, here indicates the direction of ionic motion, and simply shows whether the given positive ions tend to flow away from the metal into the solution or towards the metal from the solution. That is, whether the "solution pressure" of the metal is greater or less than the "osmotic pressure" of the ions in solution.[1]

Now, when an electropositive and an electronegative metal are coupled, the direction of flow of the ions of both through the solution is the same, and the electromotive force of the combination is the arithmetic sum of those of the ingredients. When two electropositive or two electronegative metals are coupled, the ions tend to flow through the solution in opposite directions ; hence, the electromotive force of the combination is equal to the arithmetic difference between the separate electromotive forces, the direction of motion, and hence the sign, being that of the greater.

In combinations in which the Ostwald normal electrode is one member, we know the amount and direction of one electromotive force, and hence, when we measure that of the combination, it is easy to calculate that of the other (neglecting

[1] With regard to the anions, the + and − signs have an inverse meaning.

the slight electromotive force due to the contact of the solutions).[1]

Thus, if, against the normal electrode, aluminum in a $\frac{M}{I}$ solution of potassium cyanide gives an electromotive force $=$ $+1.55$ volts,—that is, if the current flows from the aluminum to the mercury, the same as in the case of mercury,—it follows that the electromotive force of the aluminum in $\frac{M}{I}$ potassium cyanide will be $+1.55 - 0.560 = +0.99$ volts.

Again, if a strip of amalgamated zinc under similar circumstances gives a voltage of $+1.49$ volts, the electromotive force of amalgamated zinc in a $\frac{M}{I}$ potassium cyanide solution will be $+1.49 - 0.560 = +0.93$ volt.

In making the determinations, it must be evident from the formula that, if there are few ions of the given metal present in the solution at the start, the introduction of a very few more will make great changes in the value of the electromotive force.

For in log $\frac{P}{p}$ it must be evident that as P the solution tension is constant (for a given temperature), the value will depend entirely upon p, the osmotic pressure, and the smaller p is, the greater will be the effect due to slight changes in p. Hence, it will be impossible to get constant values for the electromotive force, unless the value of p is nearly constant; that is, when the solution is saturated with ions at the given temperature. That is the case with the normal electrode, where the mercury lies in a saturated solution of mercurous chloride. The mercury is thus in equilibrium with its ions, and a constant electromotive force results.

To get perfectly constant results with cyanide solutions, it would be necessary to have the solution saturated with the cyanide of the metal in question. But while this would give us a very satisfactory electromotive series, it would not give us a measure of the action of the unsaturated cyanide solu-

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[1] This, except in cases of great differences in the concentration of the solutions, has been shown to cause an error of only a few thousandths or hundredths of a volt.

tion, just as it acts on the ores. We must, therefore, be content with results that are not entirely concordant, and take the best of a large number of determinations.

The strips used were always freshly burnished with sandpaper, cooled, and touched to a grounded platinum wire to discharge any electricity with which they might have been charged in burnishing.

Preliminary Results with the Deflection Method.—The following preliminary results were obtained in October to December, 1896, with some of the common metals and minerals. The metals were good commercial articles, such as are in use in the arts, except in the case of gold, silver, and mercury, which were chemically pure. In the case of some of the minerals, such as zincblende, stibnite, etc., the electrical resistance was probably so high in comparison with that of the intercalated resistance that the results may be somewhat low.

Nevertheless, they give at once some important relations which must exist whenever the cyanide process is applied in the treatment of ores :

Table I.—Electromotive Force of Metals in Cyanide Solutions. Deflection Method. Preliminary Experiments.

Ostwald's normal electrode = —0.560 volt.

	$\frac{M}{1}$ KCN.	$\frac{M}{10}$ KCN.	$\frac{M}{100}$ KCN.	$\frac{M}{1000}$ KCN.
	Volt.	Volt.	Volt.	Volt.
*Aluminium	+0.99	+0.90	+0.76	+0.40
*Zinc, amalgamated	+0.93	+0.82	+0.70	+0.44
*Zinc, commercial	Not determ.	+0.77	+0.59	+0.39
*Copper	+0.81	+0.62	+0.37	+0.16
*Cadmium	+0.61	+0.57	+0.35	....
Cadmium,amalgama'd	+0.55	+0.31	+0.19	....
*Tin	+0.45	+0.24	+0.17	+0.06
*Bornite	+0.45	+0.25	—0.16	....
Copper, amalgamated	+0.39(?)	+0.41	—0.14(?)	—0.12(?)
*Gold	+0.37	+0.23	+0.09	—0.38
*Silver	+0.33	+0.15	—0.05	—0.36
*Copper-Glance	+0.29(?)	+0.25	+0.05	—0.44
*Lead	+0.13	+0.05	+0.01	....
Tin, amalgamated	Not determ.	+0.01	—0.07	—0.12
Lead, "	"	....	—0.03	....
*Mercury	—0.09	+0.01	—0.11	....
Gold, amalgamated	....	....	—0.13	—0.26

	Ostwald's normal electrode = −0.560 volt.			
	$\frac{M}{1}$ KCN.	$\frac{M}{10}$ KCN.	$\frac{M}{100}$ KCN.	$\frac{M}{1000}$ KCN.
	Volt.	Volt.	Volt.	Volt.
*Antimony	+0.06	+0.03	−0.03	....
*Arsenic	+0.04	−0.05	−0.21	....
*Bismuth	+0.00	−0.06	−0.20	....
Niccolite	−0.11	−0.17	−0.44	....
*Iron	−0.17	−0.24	−0.24	....
*Chalcopyrite	−0.20	−0.34	−0.44	....
*Pyrite	−0.28	−0.42	−0.48	....
*Galena	−0.28	−0.48	−0.52	....
*Argentite	−0.28	−0.56	−0.55(?)	....
Berthierite	−0.30	−0.52	−0.52	....
Speiscobalt	−0.30	−0.33	−0.50	....
Magnetopyrite	−0.30	−0.40	− 0.54	....
Fahlore	−0.36	−0.52	−0.52	....
Arsenopyrite	−0.40	−0.45	−0.54	....
*Platinum	−0.40	−0.46	−0.50	....
Cuprite	−0.43	−0.55	−0.57	....
*Electric light carbon	−0.46	−0.52(?)	−0.57	....
*Blende	−0.48	−0.52	−0.55	....
Boulangerite	−0.50	−0.55	−0.55	....
Bournonite	−0.50	−0.55	−0.56	....
Coke	−0.52	− 0.52	−0.42(?)	....
Ruby silver ore	−0.54	−0.53(?)	−0.54	....
Stephanite	−0.54	−0.55	−0.52(?)	....
*Stibnite	−0.56	−0.56	−0.56	....

The electromotive forces of the metals and minerals marked
with an asterisk in the above table have been plotted in Fig.
II. The Y axis shows the potential in volts, the X axis the
concentration in gram-molecules and also in percentages of
potassium cyanide.

It will be noticed that in most cases the curves approxi-
mate quite closely to the logarithmic curve which theory
would give, supposing the osmotic pressure of the metallic ions
present to be inversely proportional to the concentration of
the free potassium cyanide present, but they have different
origins.

It will be noticed that the electromotive force of commer-
cial sheet-zinc is increased by amalgamation, probably by re-
ducing local action with some of its impurities, by which some
of the current produced is short-circuited. In all the other
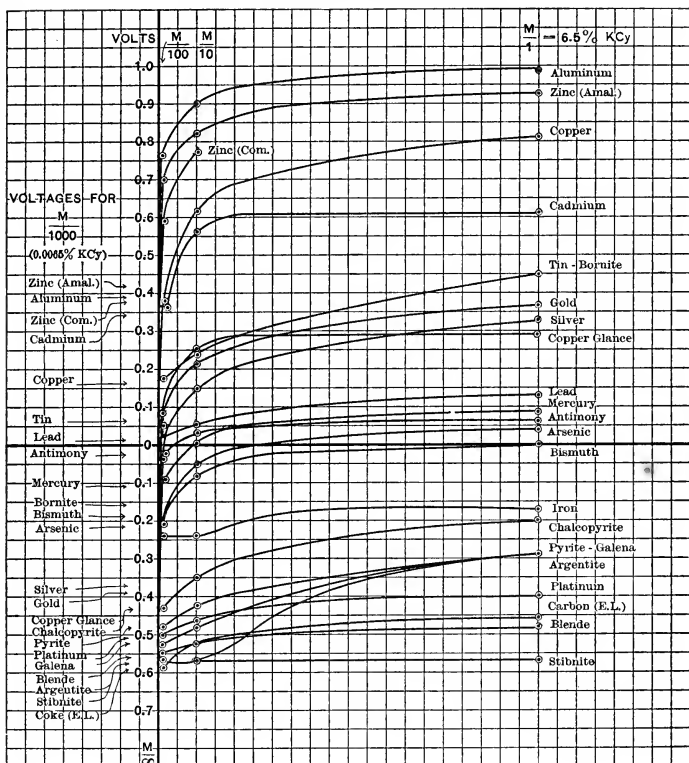
PRELIMINARY RESULTS. OCT. - DEC. 1896.
Fig. II.

experiments amalgamation reduces the electromotive force of the combination.

With some substances, particularly aluminium, copper, iron, platinum, and gas carbon, it was very difficult to get concordant results; with aluminum and copper this seemed to be due to a tendency to form an insoluble film on the surface of the

metal, which put a stop to further action. With copper and iron it was also possibly due to a tendency of the metals to a change of valency, which is accompanied by a change in the electrical state. With platinum and gas carbon it was not improbably due to a varying content of absorbed gas.

In testing the minerals, it was in all cases difficult to get a complete electrical contact between the tips of the platinum forceps and the rough surface of the mineral fragment, so that the results are only provisional, particularly as the resistance in some of these cases was very high. Nevertheless, the results are very interesting. They show, for instance, that not all copper minerals have a strong action on the current. Pure chalcopyrite, for instance, has hardly more action than pure pyrite, while bornite and copper glance have a very decided tendency to go into solution. Cuprite is also apparently very little acted on, though this may be due to its high resistance rather than to a lack of tendency to dissolve. The soluble salts and minerals of copper could not be tested in this manner, owing to their non-conductivity.

It is plain, however, that pure chalcopyrite, galena, argentite, magnetopyrite, fahlore, arsenopyrite, blende, boulangerite, bournonite, ruby silver ore, stephanite, and stibnite, when free from their oxidation-products, are apparently very little acted on by cyanide solutions.

It is also plain that a particle of metallic gold, in contact with a particle of pyrite, forms a galvanic couple in $\frac{M}{1}$ or 6.5 per cent potassium cyanide solution, equal to $+0.65$ volt, in $\frac{M}{10}$ or 0.65 per cent potassium cyanide solution, $+0.65$ volt, and in $\frac{M}{100}$ or 0.065 per cent potassium cyanide solution, $+0.57$ volt. With zinc, under the same circumstances (if we take for $\frac{M}{1}$ potassium cyanide solution the figures for amalgamated zinc), taking the zinc as the more electropositive metal, and subtracting the potential of gold, we have differences of $+0.56$ volt, $+0.54$ volt, and $+0.50$ volt. In short, these figures would measure the tendency of the zinc to

dissolve, or of the gold to precipitate in potassium cyanide solutions of these strengths.

According to these figures, the precipitating power of the zinc seems to hold up quite well for the dilute solutions. The actual failure to precipitate the gold, sometimes met with in dilute solutions, is no doubt due to films of cyanide or hydrate of zinc, which form incrustations on the surface of the zinc and thus prevent contact. The fact that the use of a small amount of fresh cyanide or of caustic potash in the zinc-boxes starts precipitation again, seems to favor this explanation.

The Zero Method.—This method is shown in outline in Fig. III. NE is the Ostwald normal electrode. B is the cell con-
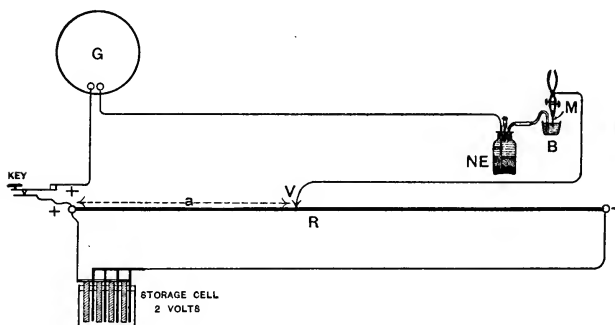
POGGENDORF'S COMPENSATION - METHOD.

B, Cell Containing Cyanide Solution;	R, Resistance Graduated into 10,000 Parts;
M, Metal to be Tested;	V, Movable Contact;
NE, Ostwald's Normal Electrode;	G, Wiedemann's Reflecting Galvanometer.

Fig. III.

taining the cyanide solution in which, as before, is immersed the metal M to be tested. At G is a galvanometer. At R is a resistance, graduated, in my experiments, into 10,000 parts. A storage battery of 2 volts and the combination cell NE–B are so connected that their positive poles are both connected at the same end of the resistance R. The negative pole of the storage battery is attached to the other end of the resistance R, so that the whole current of the storage battery discharges

constantly through R. The latter should be great enough to avoid heating, and to maintain a constant potential between the ends of R. The other terminal of the combination (the negative pole) is then moved along the resistance R till some distance, *a*, is reached at which the electromotive force of NE–B is exactly balanced by the electromotive force of the storage battery for that fraction of R represented by *a*. In this case there is no deflection of the galvanometer; at other points the galvanometer will be deflected either to the right or left, according as too much or too little electromotive force is used to balance NE–B. The electromotive force of the storage battery is, of course, first calibrated by comparing it with a standard Clark cell, placed where NE–B is.

This method of determining the electromotive force of a cell is deservedly considered one of the most reliable. With non-polarizing cells, it certainly leaves nothing to be desired. But, in investigations of this kind with cells that are easily polarized, accurate results are obtained only by a long num-ber of very tedious approximations, which render the work almost interminable. For it is, of course, impossible to hit the right balance at first, and if the connection is made at any point except the right one, the metallic electrode will receive either a positive or negative charge from the storage battery, and a true reading will be thus made impossible. It is neces-sary to change the entire solution in B, put in new electrodes at M, drive out the diffused cyanide solution from NE, and so on, until these operations have been repeated perhaps a dozen times. If this is not done the results are very unreliable. With the deflection method, on the other hand, the observa-tions may be made very rapidly, and though there is a ten-dency for the readings to be a little low unless they are quickly made, still, with a high intercalated resistance, and a delicate reflecting galvanometer, this method seems to be reliable for these quickly polarizing electrodes.

As I have already stated, and as was first pointed out by Ostwald, strictly concordant results are possible only when the electrode is surrounded with a medium already saturated with its ions.

I had intended to verify the results in Table I. with the zero method before publication, but although I had all the apparatus set up for over two years, ready to begin at any time, I was prevented from touching it by the constant pressure of routine work till shortly before the time set for the San Francisco meeting of the Institute, in September, 1899. Meantime Prof. A. von Oettingen, professor of physics in the University of Leipzig, read a very valuable paper on this subject before the Chemical and Metallurgical Society of South Africa, in January and February, 1899. In this paper he gives the results of a large number of determinations which he made of the electromotive force of metals in cyanide solutions by means of Poggendorff's compensation method, or, as I shall call it for brevity, the zero method.

Prof. von Oettingen's results are given in Table II.

The above results were all obtained by the Poggendorff compensation or zero method, the Lippmann capillary electrometer being used as an indicator instead of a galvanometer.

Prof. von Oettingen says of these results :

'' The two figures in each column refer to the first and last observations on each metal, the intermediate values being omitted. The time occupied by the change is very variable ; copper, for instance, took an hour. When no changes occur, this is indicated by a constant. The changes of potential are not always in the same direction, sometimes decreasing, sometimes increasing. But the direction of the changes in any given metal is always the same.''

It will be noticed on examining the table that this last sentence is not correct (unless there should be a typographical error in his table). For gold, silver, copper, cobalt, ferric oxide, and lead peroxide, the highest value for the same metal is sometimes the first and sometimes the second value. In the case of copper $\frac{M}{100}$ potassium cyanide the results jump from —0.212 volt to +0.380 volt,—a difference of 0.592 volt.

Table II.—Potentials of Different Metals in Contact with Potassium Cyanide Solutions at 25° C.

Experiments of Prof. A. von Oettingen, Jour. Chem. and Metallurgical Soc., South Africa, January and February, 1899.

	$\frac{M}{1}$ KCN. volt.	$\frac{M}{10}$ KCN. volt.	$\frac{M}{100}$ KCN. volt.	$\frac{M}{1000}$ KCN. volt.	$\frac{M}{100}$ KCN + $\frac{M}{0.670}$ Au. volt.
Au	+0.340 to +0.306	+0.180 to +0.218	−0.092 to −0.056	−0.414 to −0.474	−0.020 to −0.170
Ag	+0.330 " +0.314 const.	+0.176 const.	−0.020 const.	−0.340 " −0.200	−0.308 to −0.330
Cu	+0.890 " +0.924	−0.680 to +0.648	−0.212[1] to +0.380	−0.550 " −0.230	
Hg	+0.162 " +0.200	+0.008 " +0.024	+0.056 const.	......	
Ni	−0.290 " +0.194	−0.466 " −0.392	−0.550 to −0.488	−0.560	
Co	+0.182 " +0.196	+0.118 " −0.220[2]	−0.168 " −0.240	......	
Fe	+0.056 " −0.146	+0.034 " −0.012	−0.054 " +0.022	−0.008 to 0.050	
Fe₂O₃	−0.674 " −0.700	−0.796 " −0.720	−0.824 " −0.750	......	
PbO₂	+0.160 const.	+0.110 " +0.118	−0.062 " +0.070	−0.006 const.	
Pb	+0.164 const.	+0.128 const.	+0.120 const.	+0.120 "	
Zn	+0.924 " +0.940	+0.780 to +0.800	+0.560 to +0.604	+0.480 "	+0.126 const.

[1] On moving the fluid the potential suddenly rises.

[2] The potential changed suddenly from −0.121 to +0.118, then remained constant. (Note the discrepancy between −0.220 in the table and −0.121 in the footnote.)

I shall speak of the probable cause of these differences later.[1]

In order to make clearer the meaning of Prof. von Oettingen's results, I have plotted them in Fig. IV., as mine are plotted in Fig. II. In the figures, x is made to mark the molecular concentration, $\dfrac{M}{I}, \dfrac{M}{IO}, \dfrac{M}{IOO}, \dfrac{M}{IOOO}$; the y axis shows

[1] There are some other potential differences given by Prof. von Oettingen which I include here·

$$\frac{Hg}{Hg_2SO_4} = -0.99 \text{ volts. (Ostwald),} \frac{M}{I} \text{ solutions.}$$

$$\frac{Zn}{ZnSO_4} = +0.524 \quad `` \qquad `` \qquad\qquad ``$$

$$\frac{Mg}{MgSO_4} = +1.243 \quad `` \qquad `` \qquad\qquad `` \qquad 18° \text{ C.}$$

$$\frac{Cd}{CdSO_4} = +0.158 \quad `` \qquad `` \qquad\qquad `` \qquad `$$

$$\frac{Pb}{Pb(C_2H_3O_2)_2} = -0.089 \text{ volts. } `` \qquad `` \qquad\qquad ``$$

$$\frac{Cu}{CuSO_4} = -0.582 \quad `` \quad `` \qquad\qquad `` \qquad\quad ``$$

$$\frac{Ag}{Ag_2SO_4} = -1.024 \quad `` \quad `` \qquad\qquad `` \qquad\quad ``$$

$$\frac{\cdot Hg}{Hg_2Cl_2} = -0.560 \text{ (Ostwald's normal electrode).}$$

Prof. von Oettingen himself determined the following also (all at 25° C.) :

$$\frac{Au}{AuCl \text{ (conc)}} = -1.64 \text{ to } 1.42 \text{ volts, variable.}$$

$$\frac{Au}{\frac{M}{I} \ AuCl_3} = -1.134 \text{ volts.}$$

$$\frac{Au}{Aqua \ regia} = -1.09 \text{ volts.}$$

$$\frac{Au}{KCNS \text{ (sat.)}} = -0.26 \text{ to } +0.03, \text{ very variable.}$$

$$\frac{Au}{M \ KCNS} = -0.36, \text{ variable volt.}$$

$$\frac{Au}{\frac{M}{IO} KCNS} = -0.40 \text{ volt.}$$

$$\frac{Au}{KCNS \text{ (sat.)}} = +0.50 \text{ volt.}$$

$$\frac{Au}{K_2S} = +0.14 \text{ volt.}$$

$$\frac{Au}{K_2S_7} = +0.21 \text{ volt.}$$

$$\frac{Au}{Na_2S} = 0 \text{ to } 0.136 \text{ volt.}$$

$$\frac{Ag}{KCN \text{ (sat.)}} = +0.536 \text{ volt.}$$

$$\frac{Cu}{KCN \text{ (sat.)}} = +1.154 \text{ volts.}$$

$$\frac{Zn}{KCN \text{ (sat.)}} = +1.196 \text{ volts.}$$

24–27

the potential in volts. The designation Zinc 1 means that
this was the first value obtained with zinc, the designation
Zinc 2 the final value, etc. It will be noticed that sometimes
the first value is higher than the second and sometimes *vice
versa*, but the results are not consistent throughout, some-
times crossing each other.

The first curves of each metal, except mercury, approxi-
mately follow the logarithmic law (on the assumption that the
number of metal ions is inversely proportional to the potas-
sium cyanide concentration). Evidently the curves will cross
the X axis at different points, and not usually at a molecular
concentration M = 1, unless it should accidentally happen that
$\frac{P}{1} = 1$ for M = 1. The second curves of zinc, copper, gold,
and silver, also approximately follow it. But the second
curves of mercury, cobalt, nickel, and iron depart considera-
bly from it. It is possible that these departures are due to
polarization effects, as already explained. The irregularities
are much more marked than with the deflection method.
With that method, provided a sufficiently large resistance is
used, the first deflection is the greatest, and is taken as the
reading nearest to the truth. The deflection then gradually
falls (often quite rapidly, if there is a formation of gas on the
face of the electrode) ; but the electromotive force never rises
unless the first effect of the current is to produce a film of gas
or insoluble cyanide which puts a stop to the current, either
by setting up an opposing electromotive force or by prevent-
ing or reducing contact by its resistance. In this case, shak-
ing the solution or jarring the electrode usually gives an in-
crease of the electromotive force by destroying the film in
part ; but, if the metallic surface is untarnished to begin with,
the electromotive force rarely rises again to its first value.

New Method of Plotting Results.—The method of plotting
results hitherto used, while it shows very well the near ap-
proach of the curve to the true logarithmic curve, has the dis-
advantage that only three or four values for the tenth ratio
can be plotted. If, however, instead of making $x = \frac{P}{p}$, as we
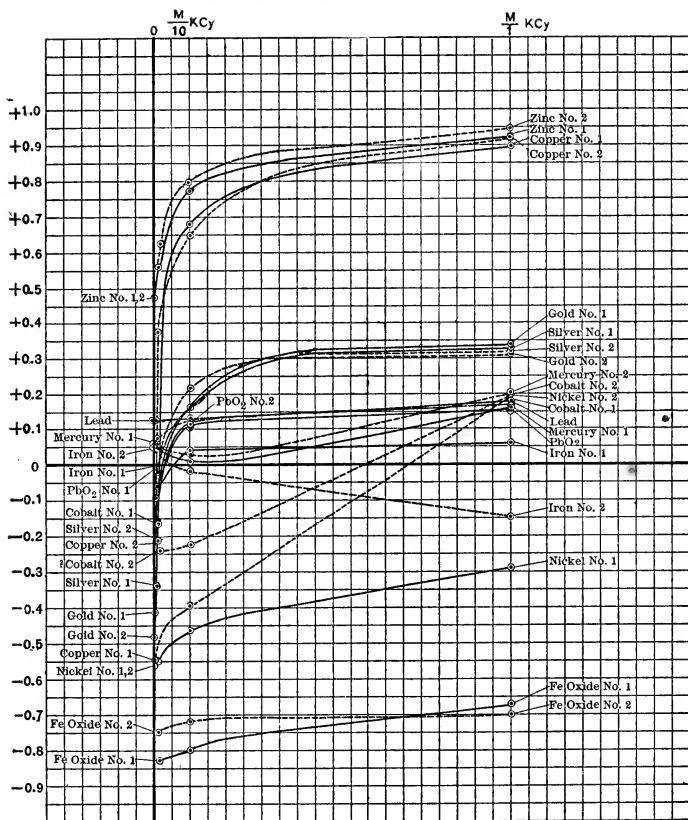
E.M.F. OF METALS IN CYANIDE - SOLUTIONS.

by Prof. *v.* Oettingen of Leipzig.

(J. Chem. & Met. Soc. S. A. Feb. 1899.)

x — M.   y = π — .058 log P/p Volts.

Fig. IV.

have done, we let $x = \log \dfrac{P}{p}$, and plot the curve $y = 0.058$

log $\dfrac{P}{p}$ volts, the curve becomes a straight line passing through the origin at o.   For $x = o$, $y = o$.

The curve is plotted in Fig. V. for values of $x = \log \dfrac{P}{p}$ from $+13$ to -12, which gives voltages from $+0.755$ to -0.696, and the table shows values from $x = \log \dfrac{P}{p} =$ minus infinity to 40.   It shows that an enormous change in the value $\dfrac{P}{p}$ is necessary to produce a very moderate change in the voltage.   Thus, to produce a change of 2.32 volts, a change in the ratio $\dfrac{P}{p} = 10^{40}$ (or ten to the fortieth power) is necessary.

In our experiments, of course, we do not know the value of $\dfrac{P}{p}$, but as a first approximation we may assume it inversely proportional to the molecular concentration $M \times 10n$.

On the axis of x is plotted the logarithm of the molecular concentration expressed in the powers of 10.   Thus, $x = \log M = \log 10^{\pm n}$.   The y axis gives the electromotive force in volts.   For comparison the theoretic formula of Nernst is also given.

If we plot Prof. von Oettigen's results, as in Fig. VI. on this plan, they become at once more intelligible.   We see at once that all the curves do not remain straight lines.   The zinc follows along very nearly in the theoretic straight line. The copper starts well, but soon falls quite rapidly, due probably to increasing dissociations.   The gold and silver approximate fairly well, also, but the rest depart from it considerably.

Comparison of the Deflection and Zero Methods.—Since the results of Prof. von Oettigen were published, I have thought best to try the zero method as well as the deflection method, and to compare the results so far obtained with each other. I have also decided to plot the results by the same method as shown in Fig. V., as it enables us to compare the results over a wider range of dilution than the former method of tabulation would cover.

NERNST'S LAW OF ELECTROMOTIVE FORCE

When x = log. P/p   y = 0.058 log. P/p Volts

Fig. V.

TABLE OF VALUES.

P/p	x = log. P/p	y = 0.058 log. P/p	P/p	x = log. P/p	y = 0.058 log. P/p
0	− ∞	− ∞ Volts	10¹	+ 1	+ 0.068 Volts
10⁰	− 40	− 2.320 "	10²	+ 2	+ 0.116 "
10⁻³⁰	− 30	− 1.160 "	10³	+ 3	+ 0.174 "
10⁻¹⁰	− 10	− 0.580 "	10⁴	+ 4	+ 0.232 "
10⁻⁹	− 9	− 0.522 "	10⁵	+ 5	+ 0.290 "
10⁻⁸	− 8	− 0.464 "	10⁶	+ 6	+ 0.348 "
10⁻⁷	− 7	− 0.406 "	10⁷	+ 7	+ 0.406 "
10⁻⁶	− 6	− 0.348 "	10⁸	+ 8	+ 0.464 "
10⁻⁵	− 5	− 0.290 "	10⁹	+ 9	+ 0.522 "
10⁻⁴	− 4	− 0.232 "	10¹⁰	+ 10	+ 0.580 "
10⁻³	− 3	− 0.174 "	10²⁰	+ 20	+ 1.160 "
10⁻²	− 2	− 0.116 "	10⁴⁰	+ 40	+ 2.320 "
10⁻¹	− 1	− 0.068 "			
10⁰	0	0 "			

After the foregoing description and discussion of the various methods employed in this investigation, the reader will be able to study intelligently the tabulated results of the tests hereinafter stated.

E.M.F. OF METALS IN CYANIDE - SOLUTIONS.
Prof. *v.* Oettingen of Leipzig. (J. Chem. and Met. Soc. S. A. Feb. 1899.)

Fig. VI.

Results of Experiments.

The following tables show, for the several methods tested, my own results, obtained at different times and by different methods, as well as those of Prof. von Oettingen. In every case each observation was made independently, without regard to the ultimate result of its reduction. But the later readings are more reliable than the earlier, because a certain knack in catching the needle at its maximum position, before the voltage begins to fall, was acquired during the work. The tables give the readings as reduced from the actual observations, without attempted correction ; but when any anomaly rendered the observation uncertain this is indicated by a(?). Such was the case particularly in the readings with distilled water (M divided by ∞), which were very uncertain, especially for easily oxidizable metals like zinc and iron.

Experiments with Commercial Sheet Zinc.—Experiments were made at different times with both the zero and the deflection method on the ordinary commercial sheet zinc, such as is actually used in making zinc shavings, for precipitating gold. The results are given in Table III., and those of Prof. von Oettingen have been introduced into the same table, for comparison.

These results are plotted together for comparison in Fig. VII. It will be evident that from $\frac{M}{I}$ to $\frac{M}{100}$, or from 6.5 to 0.065 per cent, the curve nearly follows the theoretic straight line. Curves *a*, *f*, and *g* appear to follow it to $\frac{M}{1,000}$ or 0.0065 per cent, for more dilute solutions beyond that point the curve approximates a horizontal straight line. This, according to the Nernst theory, would mean that the number of zinc ions in such solutions remains nearly constant. In spite of all the irregularities in the curves, the point —3 or $\frac{M}{1,000}$ or 0.0065 per cent potassium cyanide is evidently a critical or inflection-point in the curve.

The results obtained with high dilutions of cyanide and

Table III.—Electromotive Force of Zinc (Commercial Sheet, Burnished) in Potassium Cyanide.

Curve.	(a.)	(b.)	(c.)	(d.)	(e.)	(f.)	(g.)
Notebook B1, p.	67	176	177	186	193	Published	Published
Date	Oct. 19, '96	Aug. 30, '99	Aug. 30, '99	Sept. 4, '99	Sept. 8, '99	Feb., '99	Feb., '99
Method	Deflect.[1]	Zero.[2]	Deflect.[2]	Deflect.[3]	Deflect.	Zero.	Zero.
Resis. ohms	100,000	......	100,000	100,000	200,000	......	......
Temperature	22° C.	19° C.	19° C.	19° C.	198° C.	25° C.	25° C.
Observer	Christy	Christy	Christy	Christy	Christy	Von Oettingen	Von Oettingen
EMF (N.E.=−0.560) Concentration	Volt.	Volt.	Volt.	Volt.	Volt.	Volt.	Volt.
KCN $\frac{M}{1}$	......	+0.946	......	+0.906	+0.914[4]	+0.924	+0.940
$\frac{M}{10}$	+0.770	+0.861	......	+0.815	+0.836[4]	+0.780	+0.800
$\frac{M}{100}$	+0.585	+0.772	......	+0.730	+0.735[4]	+0.560	+0.604
$\frac{M}{1,000}$	+0.385	+0.415	+0.386	+0.300	+0.371[5]	+0.480	+0.480
$\frac{M}{10,000}$	......	+0.385(?)	+0.326	+0.270	+0.332	......	......
$\frac{M}{100,000}$	......	+0.355	+0.320	+0.270(?)	+0.332(?)	......	......
$\frac{M}{1,000,000}$	......	+0.383(?)	+0.312	+0.282(?)	+0.332(?)	......	......
$\frac{M}{\infty}$ (= H_2O)	+0.041(?)	+0.372(?)	+0.256(?)	+0.240(?) +0.350(?)	+0.293(?)	......	......

Tested from strong to weak solutions.

[1] Used same strip of zinc throughout experiments, burnishing each time.
[2] Used new burnished strip each time.
[3] Same strip, burnished each time. Tested from weak to strong solutions.
[4] Fine bubbles form on zinc and then voltage falls. Shaking causes bubbles to escape, and voltage rises.
[5] Below this no gas bubbles visible to naked eye, but voltage falls, and then rises on shaking.
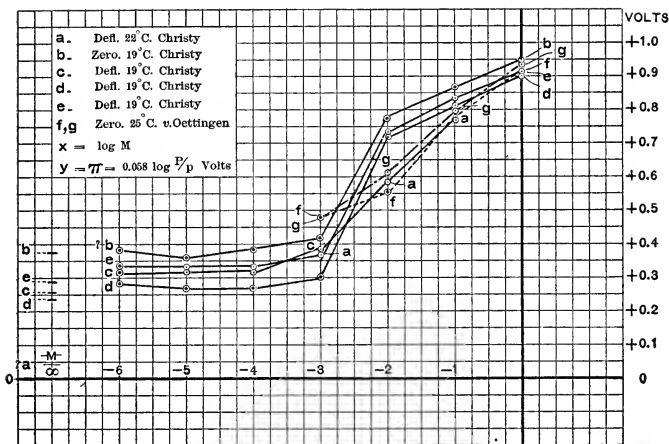
E.M.F. OF ZINC IN KCy. SOLS.

Fig. VII.—On the horizontal (x) axis are laid off the values of log $M = \log 10^n$; on the vertical (y) axis the actual volts.

with distilled water were very uncertain, probably because of the formation of insoluble films of oxide of zinc and occluded hydrogen, which prevented the accurate reading of the needle.

In my results with the deflection method, I have always taken the highest reliable reading as the most probable result. It was often quite difficult to make sure of the proper reading, as a slight insoluble film of cyanide of copper formed almost instantly, and this lowered the potential almost before a reading could be taken. On agitating the copper so as to bring it into contact with fresh solution, the potential would gradually rise to a maximum, after which, on being left at rest, it would again fall off more gradually. It is possible, also, that the tendency of copper to form cupric, as well as cuprous cyanide, may in part explain the discordant results, such, for instance, as that obtained by Prof. von Oettingen with $\dfrac{M}{100}$ potassium cyanide solution. He says in a foot-note

Table IV.—Electromotive Force of Copper (Burnished Sheet) in Potassium Cyanide.

	(a.)	(b.)	(c.)	(d.)	(e.)	(f.)	(g.)
Notebook B1, page	68	178	188	189	190	Published	Published
Date	Oct. 20, '96	Aug. 30, '99	Sept. 6, '99	Sept. 6, '99	Sept. 7, '99	Jan., '99	Jan., '99
Method	Deflect.	Zero.	Deflect.	Zero.	Deflect.	Zero.	Zero.
Resis. ohms	100,000	......	100,000	......	200,000	......	......
Temperature	23° C.	18° C.	18° C.	18° C.	19° C.	25° C.	25° C.
Observer	Christy.	Christy.	Christy.	Christy.	Christy.	Von Oettingen.	Von Oettingen.
EMF (N. E. = −0.560)	Volt.	Volt.	Volt.	Volt.	Volt.	Volt.	Volt.
Concentration:							
$KCN \frac{M}{1}$	+0.930	+0.910	+0.905	+0.811(?)	+0.860	+0.924	+0.890
$\frac{M}{10}$	+0.620	+0.731	+0.310	+0.663	+0.660	+0.680	+0.648
$\frac{M}{100}$	+0.370	+0.146	+0.310	+0.356	+0.149	−0.212	+0.380
$\frac{M}{1,000}$	+0.158	−0.104	−0.068	−0.048	−0.151	−0.550	−0.230
$\frac{M}{10,000}$	......	−0.332	−0.241	−0.230	−0.324	......	......
$\frac{M}{100,000}$	......	−0.360	−0.299	−0.272	−0.387	......	......
$\frac{M}{1,000,000}$	......	−0.426	−0.314	−0.282	−0.442	......	......
$\frac{M}{\infty}$ (= H$_2$O)	−0.560(?)	−0.444	−0.328	−0.313	−0.450	......	......
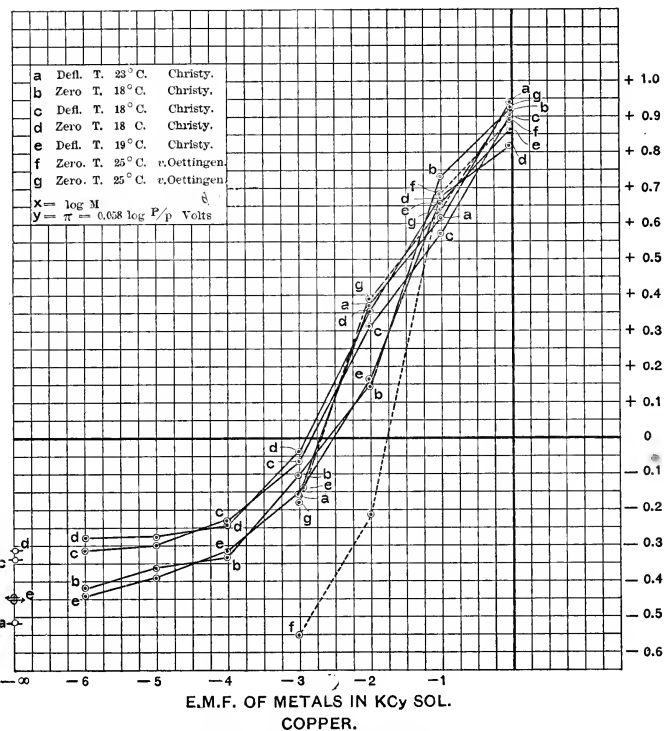
Fig. VIII.—On the horizontal (x) axis are laid off the values of log M = 10^n; on the vertical (y) axis, the actual volts.

concerning this case, "On shaking, the potential suddenly rises from —o.212 to +o.380."

The results contained in the above table have all been plotted in Fig. VIII. The mean results of these curves show a tendency to follow the course of a straight line from $\frac{M}{I}$ down to $\frac{M}{1,000}$; or perhaps to $\frac{M}{10,000}$; that is, from 6.5 down to

0.00065 per cent, when it breaks off sharply and runs along
flat again, just as the zinc curve did.

On plotting the gold curves, as has been done in Fig. IX.,
it is evident that the gold follows the logarithmic law fairly
well as far as $\dfrac{M}{100}$ or 0.065 per cent potassium cyanide. A
considerable fall of potential occurs, according to my experi-
ments, between $\dfrac{M}{100}$ and $\dfrac{M}{1,000}$, or 0.0065 per cent potassium
cyanide, indicating an increase of osmotic pressure, probably
due to an increasing dissociation of the potassium aurous
cyanide. This point seems again a critical point in the curve,
which, beyond it, runs off more flatly, indicating an approach
to a constant osmotic pressure of the gold ions.
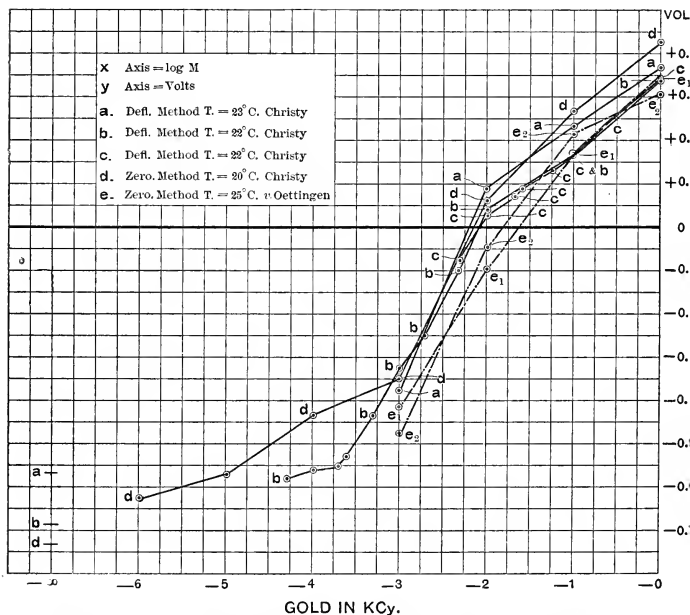
Fig. IX.—On the horizontal (x) axis are laid off the values of log $M = $ log 10^n; on
the vertical (y) axis, the actual volts.

Table V.—*Electromotive Force of Gold in Potassium Cyanide Solutions.*

	(a.)	(b.)	(c.)	(d.)	(e₁.)	(e₂.)
Curve.						
Notebook B1, page	71	86	88	172	Published Feb.,'99	Published Feb.,'99
Date	Oct. 20,'96	Dec. 12,'96	Dec. 14,'96	Aug. 26,'99		
Method	Deflect.	Deflect.	Deflect.	Zero.	Zero.	Zero.
Resis. ohms	100,000	50,000	50,000	......	......	......
Temperature	23° C.	22° C.	22° C.	20° C.	25° C.	25° C.
Observer	Christy.	Christy.	Christy.	Christy.	Von Oettingen.	Von Oettingen.
EMF (N. E. = −0.560) Concentration KCN :	Volt.	Volt.	Volt.	Volt.	Volt.	Volt.
6.4 M	......	......	+0.468	......	......	......
3.2 M	......	......	+0.420	......	......	......
1.6 M	......	......	+0.357	......	......	......
$\frac{M}{1}$	+0.366	+0.334	+0.336	+0.418	+0.340	+0.306
$\frac{M}{2}$	......	......	+0.288	......	......	......
$\frac{M}{4}$	......	......	+0.239	......	......	......
$\frac{M}{10}$	+0.233	+0.176	+0.176	+0.264	+0.180	+0.218
$\frac{M}{20}$	......	......	+0.135	......	......	......
$\frac{M}{40}$	......	......	+0.093	......	......	......
$\frac{M}{50}$	......	......	+0.073	......	......	......
$\frac{M}{100}$	+0.087	+0.045	+0.037	+0.065	−0.092	−0.056

Table V.—Electromotive Force of Gold in Potassium Cyanide Solutions (Continued).

Curve.	(a.)	(b)	(c.)	(d.)	(e.)	(f.)
$\frac{M}{200}$	......	—0.099	—0.773	......	......	......
$\frac{M}{500}$	......	—0.244	......	......	......	......
$\frac{M}{1,000}$	—0.380	—0.326	......	—0.348	—0.414	—0.474
$\frac{M}{2,000}$	......	—0.436	......	......	......	......
$\frac{M}{4,000}$	......	—0.533	......	......	......	......
$\frac{M}{5,000}$	......	—0.554	......	......	......	......
$\frac{M}{10,000}$	......	—0.560	......	—0.439	......	......
$\frac{M}{20,000}$	......	—0.581	......	......	......	......
$\frac{M}{100,000}$	......	......	—0.567	......	......	......
$\frac{M}{1,000,000}$	......	......	—0.622	......	......	......
$\frac{M}{\infty}$ (= H$_2$O)	—0.560(?)	—0.698	......			

Sept. 4,'99
Deflection
—0.724
—0.620
—0.709

Electromotive Force of Gold in Potassium Chloride and Potassium Hydroxide.

In order to bring out the effect of the potassium cyanide in reducing the osmotic pressure of the gold ions in the solution (according to the Nernst theory), I append the following experiments on the electromotive force of gold in solutions of potassium chloride and potassium hydrate. These results are given in Table VI., and are plotted in Fig. X. It is evident

Table VI.—Electromotive Force of Gold in Potassium Chloride and Potassium Hydroxide.

Curve.	(a).	(b.)
Notebook B1, page	160	159
Date	Aug. 10, '99	Aug. 10, '99
Resistance, ohms	30,000	30,000
Temperature	19° C.	18°.5 C.
Observer	Christy.	Christy.
EMF.	Volt.	Volt.
(N. E. = —0.560)		
Solution	KCl.	KOH.
Concentration :		
$\dfrac{M}{1}$	—0.487	—0.381
$\dfrac{M}{10}$	—0.510	—0.422
$\dfrac{M}{100}$	—0.523	—0.468
$\dfrac{M}{1,000}$	—0.533	—0.486
$\dfrac{M}{10,000}$	......	—0.505
$\dfrac{M}{100,000}$	......	—0.526
$\dfrac{M}{1,000,000}$	......	—0.551

that there is a very much smaller electromotive force in each of these cases. It is particularly low in the case of potassium chloride. According to the Nernst theory, the solution pressure of the gold is the same in each of these solutions ; that is, the pressure with which the gold tends to go into solution
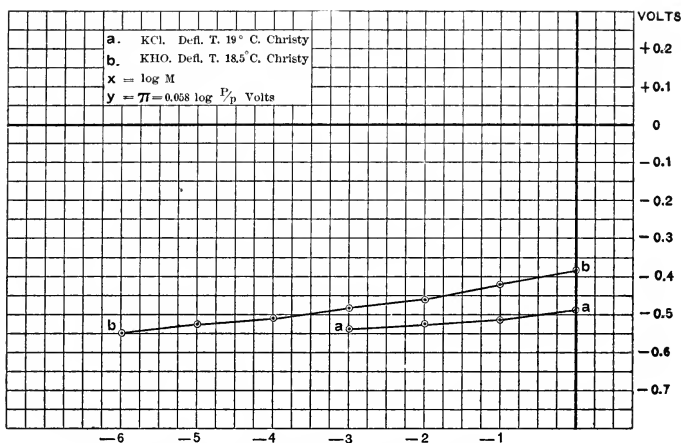
E.M.F. OF GOLD IN KCl AND KHO SOLUTIONS.

Fig. X.—On the horizontal (*x*) axis are laid off the values of log M = log 10^n ; on the vertical (*y*) axis, the actual volts.

is exactly the same (at a given temperature), whether the gold is immersed in either potassium cyanide, potassium chloride, or potassium hydrate. But the number of gold ions in each solution, and hence the resulting osmotic pressure, is very different. According to this theory, it is least in potassium cyanide, much greater in potassium hydrate, and greatest of all in potassium chloride. Consequently, the electromotive force varies inversely as p, according to the ratio $\log \dfrac{P}{p}$.

The curves in both cases run rather flat, indicating an approach to a constant osmotic pressure for high dilutions.

Table VII.—*Electromotive Force of Silver in Potassium Cyanide.*

Curve.	(a.)	(b.)	(c.)	(d.)
Notebook B1, p.	71	170	Published	Published
Date	Oct. 20,'96	Aug. 19,'99	Jan.,'99	Jan.,'99
Method	Deflect.	Zero.	Zero.	Zero.
Resistance, ohms	100,000	.....	.....	.....
Temperature	23° C.	19° C.	25° C.	25° C.
Observer	Christy.	Christy.	Von Oettingen.	Von Oettingen.
EMF (N.E. = −0.560) Concentrat'n KCN:	Volt.	Volt.	Volt.	Volt.
$\frac{M}{1}$	+0.326	+0.345	+0.340	+0.306
$\frac{M}{10}$	+0.152	+0.194	+0.180	+0.218
$\frac{M}{100}$	−0.054	+0.058	−0.092	−0.156
$\frac{M}{1,000}$	−0.360	−0.308	−0.414	−0.474
$\frac{M}{10,000}$	.....	−0.417	.....	.....
$\frac{M}{100,000}$	.....	−0.457	.....	.....
$\frac{M}{1,000,000}$	.....	−0.498	.....	.....
$\frac{M}{\infty} (= H_2O)$	−0.572	.....	.....	.....

Table VIII.—*Electromotive Force of Lead in Potassium Cyanide.*

Curve.	(a.)	(b.)	(c.)
Notebook B1, p.	68	183	Published
Date	Oct. 20,'99	Sept. 2,'99	Feb.,'99
Method	Deflect.	Zero.	Zero.
Resistance, ohms	100,000	.....	.....
Temperature	23° C.	18° C.	25° C.
Observer	Christy.	Christy.	Von Oettingen
EMF (N. E. = −0.56) Conc'trat'n KCN :	Volt.	Volt.	Volt.
$\frac{M}{1}$	+0.125	+0.200	+0.164 const.

25–27

Curve.	(a.)	(b.)	(c.)	
$\dfrac{M}{10}$	+0.050	+0.158	+0.128	"
$\dfrac{M}{100}$	+0.006	+0.112	+0.120	"
$\dfrac{M}{1,000}$	......	+0.070	+0.120	"
$\dfrac{M}{10,000}$	......	+0.046	......	
$\dfrac{M}{100,000}$	......	+0.040	......	
$\dfrac{M}{1,000,000}$	......	+0.040	......	
$\dfrac{M}{\infty}$ (= H_2O)	......	+0.040	......	
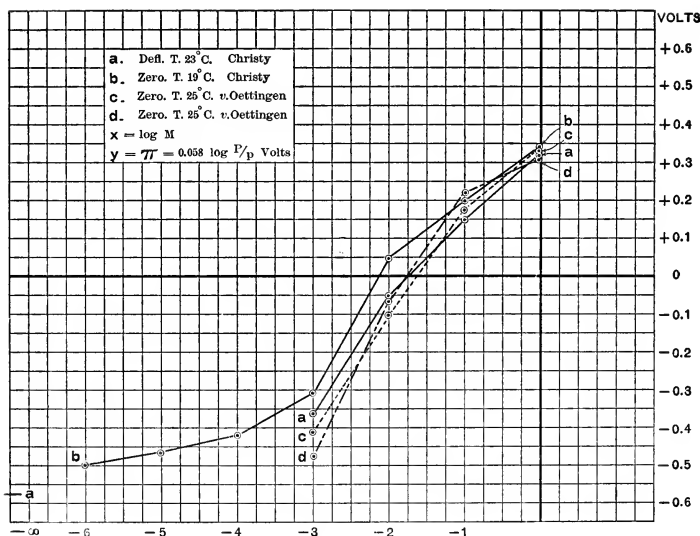
E.M.F. OF SILVER IN KCy.

Fig. XI.—On the horizontal (x) axis are laid off the values of log M = log 10^n; on the vertical (y) axis, the actual volts.

a. Defl. T. 23°C. Christy
b. Zero. T. 18°C. Christy
c. Zero. T. 25°C. v.Oettingen
x = log M
$y = \pi = 0.058 \log \text{P}/\text{p}$ Volts
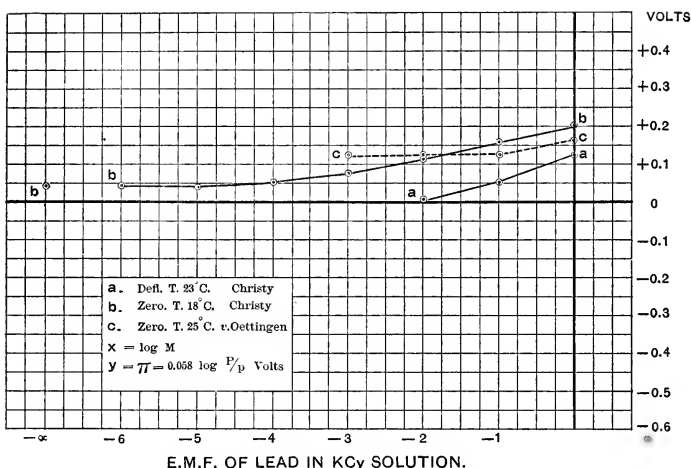
E.M.F. OF LEAD IN KCy SOLUTION.
Fig. XII.—On the horizontal (x) axis are laid off the values of log $M = \log 10^n$; on the vertical (y) axis, the actual volts.

The normal electrode, checked on $\dfrac{M}{I}$ KCl, showed —0.560, as it should do.

As a check on the foregoing results, I am able to quote the observations of an independent observer, Brandenberg.[1] He conducted a number of experiments with mercury in various depolarizing solutions. Instead, however, of using Ostwald's normal electrode, he used as one electrode mercury covered with sulphate of mercury (instead of the chloride used in Ostwald's). This electrode was then connected, by means of a siphon containing a neutral salt in solution, with a vessel containing mercury covered with the various solutions to be experimented on.

The solutions he experimented on to find their ion destroying-power, or their power to form complex ions with mercury, were: Potassium sulphide, potassium cyanide, potassium thiocyanate, sodium hyposulphite, potassium ferrocyanide,

[1] Ztschr. phys. Chem., II, 570, etc.

Table IX.—Electromotive Force of Mercury in Potassium Cyanide.

Curve.	(a.) 67 Oct. 19, '96 Deflect. 100,000 23° C. Christy.	(b.) 184 Sept. 2, '99 Zero. ...... 18° C. Christy.	(c.) 184 Sept. 2, '99 Deflect. 100,000 18° C. Christy.	(d.) Published Feb., '99 Zero. ...... 25° C. Von Oettingen.	(e.) Published Feb., '99 Zero. ...... 25° C. Von Oettingen.
Notebook B1, page Date Method Resistance, ohms Temperature Observer	Volts.	Volts.	Volts.	Volts.	Volts.
EMF (N.E. = −0.560) Concentration KCN:					
$\frac{M}{1}$	+0.091	+0.154	+0.032	+0.162	+0.200
$\frac{M}{10}$	+0.010	+0.147	−0.073	+0.008	+0.024
$\frac{M}{100}$	+0.115	−0.043	−0.176	−0.056	......
$\frac{M}{1,000}$	......	−0.193	−0.309	......	......
$\frac{M}{10,000}$	......	−0.560	−0.545	......	......
$\frac{M}{100,000}$	......	−0.664	−0.594	......	......
$\frac{M}{1,000,000}$	......	−0.705	−0.634	......	......
$\frac{M}{\infty} = H_2O$	......	−0.735	−0.640	......	......
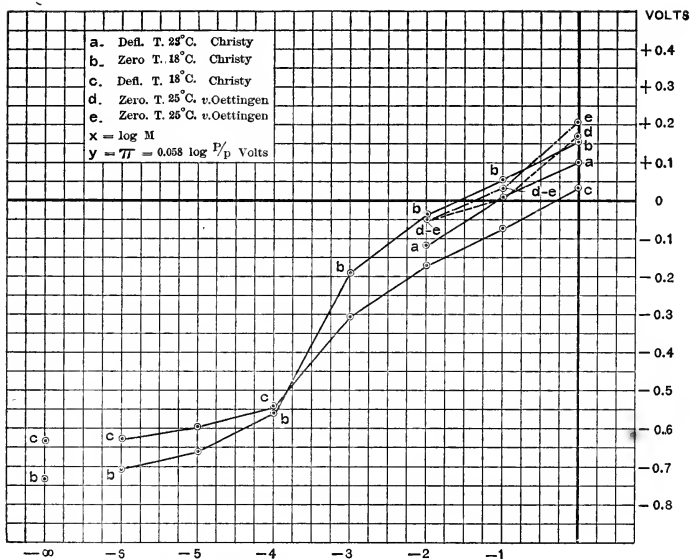
E.M.F. OF MERCURY IN KCy SOLUTION.

Fig. XIII.—On the horizontal (x) axis are laid off the values of log M = log 10^n; on the vertical (y) axis, the actual volts.

and potassium chloride. As he did not use the same strengths that I have found most convenient, I have had to plot his results, reduce them to zero potential,[1] and interpolate the results for the strengths I have used. The results so obtained are compared with the results obtained by Professor Oettingen and myself with the normal electrode. The results obtained by us for potassium cyanide are higher than Brandenberg's, but show the curves to be of the same general nature. They are shown in Fig. XIV.

[1] On the supposition that $\frac{Hg}{HgSO_4}$ has a potential of —0.98 instead of —0.560 for $\frac{Hg}{Hg_2Cl_2}$.

Fig. XIV.—On the horizontal (x) axis are laid off the values of $\log M = \log 10^n$; on the vertical (y) axis, the actual volts.

In order to bring out more clearly the nature of the relations existing between the electromotive force of the different metals, I have combined, from the plotted curves of each metal, what appear to be the most probable values for each metal. The results are contained in Table XI.

Table X.—Electromotive Force of Iron in Potassium Cyanide.

Curve.	(a.)	(b.)	(c.)	(d.)	(e.)
Notebook B1, page	68	182	180	Published	Published
Date	Oct. 21, '96	Sept. 1, '99	Sept. 1, '99	Feb. '99	Feb. '99
Method	Deflect.	Deflect.	Zero.	Zero.	Zero.
Resistance, ohms	100,000	100,000	......	......	......
Temperature	21° C.	19° C.	19° C.	25° C.	25° C.
Observer	Christy.	Christy.	Christy.	Von Oettingen.	Von Oettingen.
EMF (N. E. = −0.56)	Volt.	Volt.	Volt.	Volt.	Volt.
Concentration KCN:					
$\frac{M}{1}$	−0.169	−0.028	−0.124	+0.56	−0.146
$\frac{M}{10}$	−0.236	−0.082	−0.124	+0.34	−0.120
$\frac{M}{100}$	−0.236	−0.116	−0.124	+0.054	+0.022
$\frac{M}{1,000}$	......	−0.131	−0.124	−0.008	+0.050
$\frac{M}{10,000}$	......	−0.146	−0.124	......	......
$\frac{M}{100,000}$	......	−0.160	−0.184	......	......
$\frac{M}{1,000,000}$	......	−0.160	−0.104	......	......
$\frac{M}{\infty}$ (= H_2O)	......	−0.206	−0.104	......	......

E.M.F. OF IRON IN KCy SOLUTION.

Fig. XV.—On the horizontal (*x*) axis are laid off the values of log M = log 10ⁿ : on the vertical (*y*) axis, the actual volts.

Table XI.—Electromotive Force of Metals in a Solution of Cyanide of Potassium.

Concentration.		Combination of most probable values.			
M = Ion.	Log. Ion.	Zinc.	Copper.	Gold.	Silver.
$M = 10^{0}$	0	+0.945	+0.930	+0.420	+0.340
$M = 10^{-1}$	—1	+0.870	+0.680	+0.265	+0.195
$M = 10^{-2}$	—2	+0.775	+0.430	+0.090	+0.055
$M = 10^{-3}$	—3	+0.415	—0.050	—0.340	—0.310
$M = 10^{-4}$	—4	+0.385	—0.250	—0.450	—0.420
$M = 10^{-5}$	—5	+0.355	—0.270	—0.565	—0.460
$M = 10^{-6}$	—6	+0.330	—0.280	—0.620	—0.495
Dist. water	—∞	+0.280	—0.320	—0.720	—0.570
		Lead.	Mercury.	Iron.	
$M = 10^{0}$	0	+0.200	+0.150	—0.030	
$M = 10^{-1}$	—1	+0.160	+0.050	—0.090	
$M = 10^{-2}$	—2	+0.110	+0.040	—0.120	
$M = 10^{-2}$	—3	+0.070	—0.190	—0.130	
$M = 10^{-4}$	—4	+0.050	—0.590	—0.140	
$M = 10^{-5}$	—5	+0.040	—0.600	—0.150	
$M = 10^{-6}$	—6	+0.040	—0.635	—0.160	
Dist. water	—∞	+0.040	—0.640	—0.200	
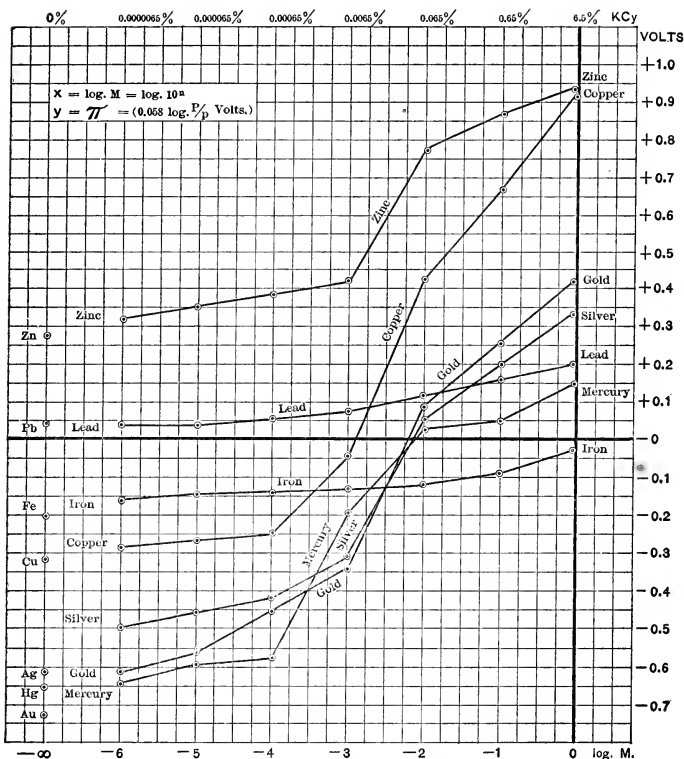
ELECTROMOTIVE FORCE OF METALS
IN POTASSIUM CYANIDE.
Combination of Most Probable Values.

Fig. XVI.

These results have been plotted in Fig. XVI. These curves all show critical points at either log M = —2, —3, or —4. Most of them show the greatest amount of inflection at log M = —3. In fact, most of them seem to change in character at this point. According to the Nernst-Ostwald theory,

this would be explained by the assumption that below say $\frac{M}{1,000}$ KCN, the dissociation of the complex ion containing the metal in point is practically complete, so that the osmotic pressure p of the given metallic ions in the dilute solutions becomes practically constant below this point, so that as the ratio $\frac{P}{p}$ is nearly constant, so its logarithm, and hence the voltage becomes also nearly constant, as is shown in the figure.

The curves for lead and iron are very remarkable; at first quite low, they maintain themselves at a higher level than either of the other metals except zinc. This is explainable on the supposition that the values of P for lead and iron are for these metals rather low, but that the values of p reach a nearly constant value sooner than for the other metals, so that the resulting curves flatten earlier.

These curves also show a number of remarkable crossings. Copper, which starts at a voltage slightly less than that of zinc, rapidly falls off, crosses the curve of lead a little below log M = —2.5, and that of iron a little before log M = —3.5, and then remains permanently below these metals. The gold curve crosses the curves of mercury, silver, and iron at just about log M = —2.5. Gold and silver both cross mercury again at about log M = —3.5. Gold finally crosses mercury again at a point beyond log M = —6, and remains permanently below it after that.

It will be observed that the metals change their sequence from that of zinc, copper, gold, silver, lead, mercury, iron, which they possess in a $\frac{M}{I}$, or 6.5 per cent potassium cyanide solution, to the order zinc, lead, iron, copper, silver, mercury, gold, in distilled water, which is the usual electrochemical series in acid solutions quoted by Wilson, except that iron is placed above lead. The determination of iron in my experiments was not entirely satisfactory, by reason, apparently, of the formation of films, and the results are probably too low. Water, also, appears to act like a weak alkali.

All the metals show a critical point somewhere between log M = —3 and —4, at which dilution they seem to change from the voltage due to the cyanide solution to that which they ordinarily possess.

From a study of these curves there seems to be little support for the so-called "selective affinity" of dilute cyanide solutions for gold and silver, except in the case of copper down to log M = —4, or 0.00065 potassium cyanide.   In the case of zinc, lead, iron, and mercury the strong solutions give a better relative voltage in favor of the gold than do the dilute cyanide solutions.   But in the case of copper there seems to be a distinct advantage in favor of the gold in dilute solutions down to 0.00065 per cent.   Then the curves widen again. These facts will appear from the following table taken from the figure :

Table XII.—Differences in Electromotive Force between Gold and Copper in Solutions of Potassium Cyanide.

Log M = log 10^n.	Value of 10^n.	KCN. Per cent.	Difference between gold and copper. Volts.
0	1 ÷ 1	6.5	0.51
—1	1 ÷ 10	0.65	0.42
—2	1 ÷ 100	0.065	0.32
—3	1 ÷ 1,000	0.0065	0.30
—4	1 ÷ 10,000	0.00065	0.20
—5	1 ÷ 100,000	0.000065	0.30
—6	1 ÷ 1,000,000	0.0000065	0.34
—∞	1 ÷ Infinity (H_2O)	0.0	0.40

It should be remarked that if we had an independent method of determining the number of metallic ions in cyanide solutions, and were thus able to plot the electromotive force in terms of the actual ionic concentration instead of the molecular concentration, we should probably reach a more perfect agreement with the logarithmic law than in the curves here shown.   Nevertheless, even as it is, a general agreement is certainly evident.

Relation between the Strength of Cyanide Solutions and Their Dissolving Power.

It has already been shown by Maclaurin[1] that the dissolving power of a cyanide solution saturated with oxygen, increases with its strength until a strength of 5 or 10 per cent is reached, and diminishes again as the strength in cyanide increases beyond that point. But, so far as I am aware, no one has proposed the question : "At what point of dilution does the cyanide solution cease to act on the gold?"

According to the Nernst theory, gold should cease to dissolve in cyanide solutions, provided no force acts except its own solution pressure, at the point at which its electromotive force is zero, for then its solution pressure will be just balanced by the osmotic pressure of the ions already in solution. At this point (provided no other force acts) the solution of the gold should cease.

It seemed interesting to ascertain if there was such a point. In order to do so it was necessary to expose the gold to the cyanide solution, in the presence of air, under circumstances most favorable for rapid solution. Hence I devised a rotating apparatus, consisting of three pairs of rollers, driven by a small Pelton water motor, on which a couple of 2.5 liter bottles, such as are used for holding nitric acid, could be laid and rotated about their long axes. The number of revolutions of the middle axis being recorded, the distance traveled was known. This precaution was taken to be able to allow for the irregularities of the motor.

Standard strips of fine gold were prepared by repeated precipitation with sulphurous acid from a diluted chloride solution. These were rolled out thin and cut to a standard size of 2 in. by $\frac{1}{4}$ in. They weighed from 250 to 330 milligrams, according to their thickness. The strips were boiled in sulphuric and muriatic acids, washed, and ignited before use. The first set of experiments was undertaken with 2 liters of solution and 0.5 liter of air, the bottles being stoppered. The weighed gold strips were then added, the bottles were rotated for twenty-four hours, and the strips were then washed and

[1] J. Chem. Soc., **63**, 731.

dried and weighed again. The number of rotations made in twenty-four hours ranged from 4,000 to 24,000, and as the interior diameter of the bottles was 4.5 inches, the distance traveled in this time by the gold strip was from 1 to 6 miles. It was impossible to get a uniform rotation rate, owing to constant changes in the water supply. But so long as the solution was kept gently agitated these variations did not seem to have any appreciable effect on the result.[1]

Table XIII. shows the results of these experiments. The first pair were undertaken with distilled water, to see if there was any loss due to erosion. The apparent loss of 0.01 milligram was almost at the limit of accuracy of the balance, but seemed to show the possibility of a slight loss due to that cause. It will be observed that up to $\frac{M}{2,000}$, or 0.00325 per cent, the gold loss is merely nominal, never more than 0.29 milligram, often zero, and the results vary in the most irregular manner. No. 18, with $\frac{M}{10,000}$, or 0.00065 per cent, gave a loss of zero, and No. 20, with $\frac{M}{4,000}$, or 0.0016 per cent, only 0.08 milligram. It is believed that these smaller losses below $\frac{M}{4,000}$ were chiefly mechanical. It was noted that while most of the bottles used were perfectly smooth inside, some seemed to have small sharp grains of sand, or slivers of glass, projecting above the smooth inner surface. In many cases it was impossible to detect these without breaking the bottles. The loss in No. 12, which was not rotated, cannot be set down to this cause. The explanation in this case, and perhaps in some others, may have been an imperfect mixing of the solution. The solutions were made up by adding the proper volume of strong solution to the proper amount of distilled water. In case the mixture of the solutions was not thoroughly made before the gold strip was added, the gold would at first lie in a layer of stronger solution that might have a slight solvent

Table XIII.—Solubility of Gold in Cyanide of Varying Strength.

In twenty-four hours. Gold strips, standard size. Fine gold, 2 in. $\times \frac{1}{4}$ in. Weight, 250 to 330 mg. $2\frac{1}{2}$ liter bottles, $4\frac{1}{2}$ in. in diameter, making 4,000 to 24,000 revolutions in twenty-four hours, and containing 2 liters cyanide solution and $\frac{1}{2}$ liter air.

No.	Strength of cyanide.	KCN. Per cent.	Revolutions in 24 hours.	Loss gold in 24 hours. Milligrams.	Remarks.
1	$\dfrac{M}{\infty} = (H_2O)$	......	24,461	0.01	
2	$\dfrac{M}{\infty} = (H_2O)$	......	13,595	0.01	New strip
3	$\dfrac{M}{100,000}$	0.000065	15,403	0.01	
4	$\dfrac{M}{100,000}$	0.000065	10,344	0.008	$\frac{24}{46}$ of 0.2 milligram, the loss in 46 hours
5	$\dfrac{M}{60,000}$	0.000109	23,750	0.00	
6	$\dfrac{M}{50,000}$	0.00013	14,430	0.00	
7	$\dfrac{M}{50,000}$	0.00013	11,315	0.06	
8	$\dfrac{M}{40,000}$	0.00016	7,920	0.02	
9	$\dfrac{M}{40,000}$	0.00016	8,490	0.11	
10	$\dfrac{M}{40,000}$	0.00016	10,180	0.19	
11	$\dfrac{M}{30,000}$	0.000216	14,850	0.02	
12	$\dfrac{M}{30,000}$	0.000216	Not rotated	0.11	
13	$\dfrac{M}{30,000}$	0.000216	8,030	0.29	
14	$\dfrac{M}{20,000}$	0.000325	6,490	0.20	
15	$\dfrac{M}{20,000}$	0.000325	17,746	0.01	$\frac{24}{45}$ of loss in 45 hours
16	$\dfrac{M}{20,000}$	0.000325	17,746	0.025	Same as above

No.	Strength of cyanide.	KCN. Per cent.	Revolutions in 24 hours.	Loss gold in 24 hours. Milligrams.	Remarks.
17	$\dfrac{M}{10,000}$	0.00065	9,780	0.08	Treated 24 hrs.
18	$\dfrac{M}{10,000}$	0.00065	9,780	0.00	Duplicate of No. 17
	Total loss, Nos. 3 to 18, inclusive			1.133	Average loss, 0.07 mg.
19	$\dfrac{M}{4,000}$	0.0016	14,423	0.26 ⎞	Mean loss, 0.17 mg.
20	$\dfrac{M}{4,000}$	0.0016	14,423	0.08 ⎠	
21	$\dfrac{M}{2,000}$	0.00325	14,423	9.68	
22	$\dfrac{M}{1,000}$	0.0065	4,260	24.86 ⎞	Mean of two, 23.03 mg.
23	$\dfrac{M}{1,000}$	0.0065	4,260	21.21 ⎠	
24	$\dfrac{M}{500}$	0.013	5,790	81.74 ⎞	Mean of two, 84.60 mg.
25	$\dfrac{M}{500}$	0.013	5,790	87.48 ⎠	
26	$\dfrac{M}{100}$	0.065	5,270	143.64 ⎞	Mean of two, 146.91 mg.
27	$\dfrac{M}{100}$	0.065	5,270	150.18 ⎠	

effect until the dilution was effected by rotation. The fact that the mean loss up to $\dfrac{M}{10,000}$ is only 0.07 milligram; that even at $\dfrac{M}{10,000}$ (Experiment No. 18), no loss, and in No. 20 a loss of only 0.08 milligram was obtained, renders it extremely probable that the solution loss up to $\dfrac{M}{10,000}$, or 0.00065 per cent, is absolutely nil. This much is certain: These experiments demonstrate that for all practical purposes the cyanide of potassium solution ceases to act at a strength below 0.001 per cent.

Going to higher strengths we find a sudden jump at $\dfrac{M}{2,000}$;

here the loss has risen to 9.68 milligram, and beyond this it rapidly increases, the strips in the $\frac{M}{100}$, or 0.065 per cent solution being eaten through in twenty-four hours.

The next set of experiments was devised to show the effect of a smaller volume of cyanide solution and an unlimited supply of air. The same bottles as before were used, but they contained only 500 cc. of solution, and were left open to the air so that the latter was free to enter. The results, as shown in Table XIV., are in general the same as before. No appreciable loss occurs up to $\frac{M}{2,000}$, but at that point, and for greater strengths, the loss rapidly increases, finally rising a little higher than before. In experiments Nos. 4 and 6 the entire solution was filtered and the washed filter was scorified and cupelled. In No. 4, where the gold-loss was 0.07, none was found. In No. 6 (the loss being 0.23 milligram), 0.02 milligram of abraded gold was found. Whether the rest was fine enough to pass the filter or was dissolved before the strong solution was diluted, is a conjecture.

The next experiments were made without agitation and in the following manner : The gold strips were suspended in perforated glass tubes just below the surface of the solution, so that although the solution was at rest, circulation by convection was possible. The volume of the solution was 250 cc. The time of action was in each case forty-eight hours. The losses are given in Table XV. ; they are somewhat smaller than before, and again negligible below $\frac{M}{1,000}$. In this case $\frac{M}{2,000}$ was not determined. The advantage of the position near the surface near the air is well shown in comparing Nos. 5 and 8. When the gold was suspended near the surface of a $\frac{M}{400}$ solution, the loss was 21.44 milligrams in forty-eight hours, or nearly 0.5 milligram per hour ; when the strip was put at the bottom of the same volume of a similar solution, the total loss in the same time was only 8.70 milligram, or hardly one-third as much.

Table XIV.—Solubility of Gold in Potassium Cyanide of Varying Strengths in Twenty-Four Hours.

Standard fine gold strips, 2 in. $\times \frac{1}{4}$ in. Weight, 250 to 330 mg. $2\frac{1}{2}$-liter bottles, $4\frac{1}{2}$ in. diameter, making 4,000 to 24,000 revolutions in twenty-four hours. Half a liter cyanide solution, 2 liters air. Freely open to air.

No.	Strength of cyanide.	KCN. Per cent.	Revolutions in 24 hours.	Gold loss in 24 hours. Milligrams.
1	$\dfrac{M}{\infty}(= H_2O)$	......	5,110	0.01
2	$\dfrac{M}{\infty}(= H_2O)$	......	5,110	0.00
3	$\dfrac{M}{12,800}$	0.0005	8,440	0.43 (!)
4	$\dfrac{M}{12,800}$	0.0005	6,600	0.07[1]
5	$\dfrac{M}{6,400}$	0.001	8,440	0.19
6	$\dfrac{M}{6,400}$	0.001	6,600	0.23[2]
7	$\dfrac{M}{4,000}$	0.0016	6,790	0.16
8	$\dfrac{M}{3,200}$	0.002	5,450	0.44
9	$\dfrac{M}{2,000}$	0.00325	6,790	1.77
10	$\dfrac{M}{1,600}$	0.004	5,450	4.29
11	$\dfrac{M}{800}$	0.008	5,540	48.43
12	$\dfrac{M}{400}$	0.016	5,540	74.96
13	$\dfrac{M}{200}$	0.0325	28,230	150.54
14	$\dfrac{M}{100}$	0.065	28,230	168.12

[1] In order to see whether or not these losses might not be due in part, or wholly, to abrasion, the solution was filtered and the filter scorified and cupelled. No gold was found in the filter.

[2] This solution was also treated as above, and 0.02 milligram of abraded gold was found.

26–27

Table XV.—Solubility of Gold in Potassium Cyanide of Varying Strength in Forty-Eight Hours. At Rest.

Standard fine gold strips 2 in. $\times \frac{1}{4}$ in. Weight, 250 to 330 milligrams. Suspended in open glass tubes, near surface, of 250 cc. Cyanide solution at rest, but so that convection currents were possible.

No.	Strength of cyanide.	KCN. Per cent.	Gold loss in 48 hours. Milligrams.
1	$\dfrac{M}{100,000}$	0.000065	0.00
2	$\dfrac{M}{10,000}$	0.00065	0.06
3	$\dfrac{M}{1,000}$	0.0065	4.33
4	$\dfrac{M}{800}$	0.008	3.8
5	$\dfrac{M}{400}$	0.016	21.44[1]
6	$\dfrac{M}{200}$	0.0325	57
7	$\dfrac{M}{100}$	0.065	42.79

All these results have been plotted together with the voltage of the gold in curves, *a*, *b*, *c*, and *d* in Fig. XVII. According to the voltage curve the voltage becomes zero for a cyanide solution of 0.00675 M, or about 0.044 per cent, and it is a curious fact that this is very near the limit of strength that practice has so far justified. Nevertheless, solutions as low as 0.01 per cent, and even less, have been employed in practice, and my experiments show that the solution acts perceptibly down as low as $\dfrac{M}{2,000}$, or 0.00325 per cent, and perhaps to $\dfrac{M}{4,000}$, or 0.0016 per cent potassium cyanide.

An Apparent Contradiction.—Although it will be seen that the solubility curves follow very closely the voltage curve, the fact that action does not cease for the zero of potential of gold in potassium cyanide solution seems to contradict the Nernst

[1] 8. A similar experiment with same conditions as to strength and volume of solution as No. 5, only that the strip of gold rested at the bottom of the vessel, gave a gold loss of only 8.7 milligrams.

VOLTAGE AND SOLUBILITY OF GOLD IN POTASSIUM CYANIDE.

Mining Laboratory, University of California, Jan. 1897.

a. Voltage Curve in KCy.
b. Gold dissolved in 24 hrs. from 2″ x ¼″ strips of fine Gold, 5000 to 8000 rev., 2.5 L. Bot. ½ L. KCy. Open to air.
c. Gold dissolved in 24 hrs. from 2″ x ¼″ strips. 2.5 L. Bot. 2 L. KCy, ½ L air.
d. Gold dissolved from Normal strips in ½ L. KCy, at rest, but suspended near surface, in 48 hours.
T. = 15° to 20° C.

Fig. XVII.—The values of M KCN on the lower margin, and the corresponding percentages of KCN at the top, belong to each fourth vertical line (i. e. to the fourth, eighth, twelfth line, etc.) of subdivision. These lines should have been made heavier in the engraving.

law. But this contradiction is only apparent and not real. It is part of the new theory that (except the infinitesimal amounts necessary to produce the state of static tension) ions cannot come into existence or disappear except in pairs. That is, for every ion with a positive charge of electricity

there must be one with an equal negative charge. Hence, when a positive ion appears another positive ion must disappear, or else a negative one must also appear simultaneously. (In the case of ions with varying valency, an ion having a double or triple valency is, of course, equivalent to two or three oppositely electrified univalent ions.)

For instance, in my experiments for determining the electromotive force of gold in potassium cyanide solution against the normal electrode, the couple is composed of

$$\frac{\text{Gold : KCN}}{\text{KCl,HgCl : Hg}}.$$
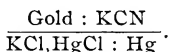
When the gold dissolves, the positive gold ions travel from the gold with their positive charge, and in order that the solution may continue, a similar flow of positive ions must continue by means of potassium ions through the solution to the mercury. The potassium ions finally drive out some of the mercury ions which precipitate into the mercury forming the electrode, at the same time giving up their charge of positive electricity to it. Simultaneously there is a corresponding flow of negative ions in the opposite direction. Thus; first chlorine and then cyanogen move in the opposite direction to meet the gold, and the latter forms with the cyanogen the complex negative ion $(Au(CN)_2)(-)$. Thus: $Au(+)+CN(-)+CN(-)=(Au(CN)_2)(-)$.

The action of this couple will go on so long as the electromotive force of the combination is greater than zero, and, as we have seen in my experiments, long after the electromotive force of the gold in the dilute cyanide solution has become zero. For the tendency of the mercury ions to discharge into the mercury electrode, can only affect its purpose and cause a current by the simultaneous solution of the gold. That is, the tendency of the positively electrified ions of mercury to discharge themselves can cause the gold to dissolve long after its own electromotive force has ceased.

The Electromotive Force of the Oxygen of the Air the Sufficient Cause of the Solution of Gold in Cyanide Solutions.

We have another substance at hand with a great tendency

to form negative ions. This is the oxygen of the air. In the presence of water, the molecule of oxygen, O_2, tends to assume the ionic state, combining with water to form four negatively electrified ions, thus: $O_2(\pm)+2H_2O(\pm)=4(OH)(-)$. Or, as has been suggested by Traube, when metals dissolve in the presence of oxygen, a molecule of the latter combines directly with 2 atoms of potentially nascent hydrogen, thus: $O_2 + 2H = H_2O_2$. Later, the peroxide of hydrogen dissociates into two negative hydroxyl ions, which, entering the solution with their negative charges of electricity, tend to produce a current in the same direction as the positively electrified mercury ions do when they leave the solution. That is, oxygen can play the same part in causing the solution of the gold as the mercury ions did in the normal electrode above cited.

The controlling importance of an abundant supply of oxygen is well shown by the curves in Fig. XVII. In curve *c*, although there is only one-fourth as much cyanide present as in curve *b*, the amount of gold dissolved is greater, except for the very dilute solutions. The evident reason that the aeration is greater. The cyanide supply being ample in both cases, the oxygen supply determines the rate of solubility. For dilute solutions, the amount of dissolved oxygen being sufficient in *b*, the greater volume of cyanide is the determining factor, and the amount dissolved in *b* is in this case greater than in *c*.

Interesting confirmation of these views is found in Maclaurin's experiments on the solubility of gold in a solution of cyanide of potassium saturated with oxygen.[1] He conducted two sets of experiments with gold strips in solutions of different strengths. The first set was left at rest for three hours, the second set was agitated. The losses are given in the following table:

Table XVI.—Maclaurin's Table of Losses of Gold in Potassium Cyanide Saturated with Oxygen.

At rest in solution saturated with oxygen. Time, three hours.

KCN, per cent	1	5	10	20	30	40	50
Gold loss, mg.[2]	8.45	13.55	15.40	11.15	8.55	5.8	5.05

[1] J. Chem. Soc., **63**, 713.
[2] Curve A, Fig. XVIII.

Agitated for two hours in solution saturated with oxygen.

KCN, per cent	1	4.9	9.4	19.93	29.5	39	10.8
Gold loss, mg.[1]	18.7	47.2	39.1	31.4	21.1	14.2	10.8

Maclaurin deems the results in the second table more relia-
ble than those in the first.   In both it will be seen that there
is a rapid increase of the dissolving power up to about 5 or 10
per cent potassium cyanide, then it gradually falls off till at
50 per cent the solubility of the gold is less than at 1 per cent.

The importance of the remarkable relation thus discovered
by Maclaurin has, I think, never before been appreciated.   Is
it not a little remarkable that the strong cyanide solution
should dissolve less gold than a weak one, while the electro-
motive force of the gold goes on steadily increasing?

But in the light of the new theory the reason is not far to
seek, for at no time does the electromotive force of the gold
rise high enough to displace without external aid any other
positive ions, such as those of the potassium in the cyanide or
the hydrogen in the water, and unless this is done the gold
ions cannot continue to form, nor the gold to dissolve.   For
this reason (as Maclaurin, myself, and others have shown),
in the absence of oxygen or some equivalent agency, gold
does not dissolve in cyanide solutions.   In other words, un-
less some negative ion like $(OH)(-)$, $(Cl)(-)$, or $(Br)(-)$
is added, or some other positive ion as $(K)(+)$, etc., is re-
moved by some external source of energy, the action cannot go
on.   Ordinarily, the oxygen of the air furnishes this energy;
as we have seen above, it dissolves in the solution and fur-
nishes the negative ions necessary to cause the solution of the
gold.

Again, Maclaurin has found the key to the anomalous ac-
tion of strong cyanide solutions.   It is in the fact which he
demonstrated, that oxygen is less soluble in strong than in
weak cyanide solutions.   The following results for the solu-
bility-coefficient of oxygen in potassium cyanide are plotted
from the curves by interpolation:

[1] Curve B, Fig. XVIII.

Table XVII.—Solubility of Oxygen in Solutions of Potassium Cyanide at 18° C. (Maclaurin.)

Strength KCN, per cent	1	5	10	20	30	40	50
Solubility, per cent	0.0295	0.0235	0.019	0.014	0.0103		
Solubility, per cent[1]	0.0290	0.022	0.018	0.013	0.008	0.005	0.003

I have replotted the results of the above experiments of Maclaurin so as to make them more comparable with my own results. I have replotted both the gold losses of Maclaurin and the second of his oxygen solubility coefficients in Fig. XVIII, and I have also added the voltage curve for gold from my own experiments.

It is plain now, for the first time, why there should be a maximum solubility somewhere between 5 and 10 per cent. There are two causes at work tending to dissolve the gold. First, the electromotive force of the gold itself, which alone is insufficient for the purpose ; and second, that of the hydroxyl ions. If we suppose the latter proportional to the solubility of the oxygen, we see that the two forces operating to cause the solution of the gold tend to increase in inverse relation. Further, that the electromotive force of the gold rises very rapidly till it gets to between 5 and 10 per cent, and then rises very slowly after that, so that it has little effect on the solubility beyond that point. The solubility of the oxygen (and, as we have assumed, of the hydroxyl ions) is a maximum for pure water, and sinks as the gold voltage rises. It is at between 5 and 10 per cent that these two factors give their maximum effect. Beyond that point, the solubility curves of the solution for oxygen and for gold run along nearly parallel.

Neither of these two factors alone is able to account for the maximum point in the solubility curve. If the presence of oxygen were the only cause, the maximum solubility would be with dilute solutions. If it were alone due to the electromotive force of the gold, it would be greatest in strong solutions. As both act together, the maximum effect lies between these extremes.

[1] Curve C, Fig. XVIII.

SOLUBILITY OF GOLD AND OXYGEN IN KCy,

From experiments of Maclaurin. (J. Chem. Soc. 1893, pg. 724.)
Replotted, and Gold Voltage - Curve Added.

Fig. XVIII.
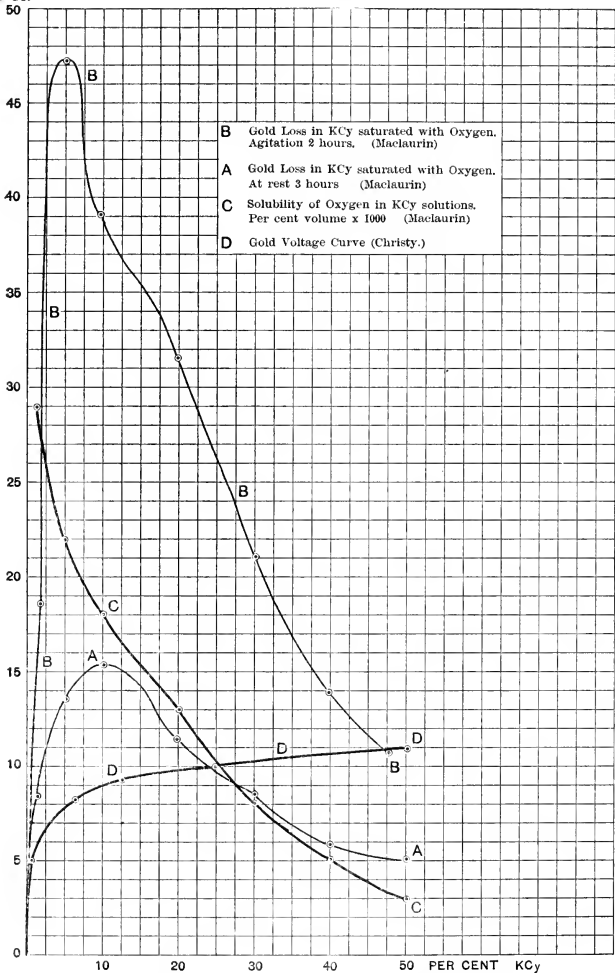
As far as I am aware, this inverse relation between the electromotive force of gold and that of oxygen in cyanide solutions of varying strength, as a controlling factor in determining the solubility of gold in such solutions, has never been brought out before. In a certain sense it is a turning-point in this discussion, and hence merits a little close attention.

The ionizing tendency of oxygen has been measured by a cell containing a platinum electrode made absorbent for oxygen by coating it with platinum sponge.[1] When this is immersed in oxygen at atmospheric pressure, and the end of the wire is immersed in $\dfrac{M}{1}$ sulphuric acid, and the latter is connected with the normal electrode, the mercury dissolves, and a positive current flows through the solution from the mercury to the platinum with a potential of $+0.75$ volt.

This current moves in the opposite direction to that due to the electromotive force of the mercury, *viz.*: -0.560 volt; consequently, the electromotive force of the oxygen at atmospheric pressure in contact with platinum sponge in $\dfrac{M}{1}$ sulphuric acid is equal to the sum of these, or 1.31 volts. It is negative, or -1.31 volts, since negative ions are produced, and the solution is negatively electrified by them.

If the above determination is correct, it follows that if, instead of the normal electrode in the above combination, we place a vessel containing a gold electrode and a solution of cyanide of potassium so weak that the potential of the gold is not merely zero, but as low as that of the mercury, *viz.*, -0.560, it is plain that a similar voltage of $+0.75$ should exist; but in this case the gold would dissolve instead of the mercury, and the positive current would flow through the solution from the gold to the platinum, as before. In this case it would be, of course, necessary to interpose an $\dfrac{M}{1}$ solution of K_2SO_4, KCl, or some other neutral salt, between H_2SO_4 and the KCN, to prevent their direct action with each other from interfering with the mere transfer of electromotive forces at the end of the line which we wish to effect.

[1] LeBlanc: "Electrochemistry," p. 221.

Now gold does not absorb and ionize oxygen as readily as platinum does, but it acts similarly, though to a much less extent. In order to test the correctness of these views, I took
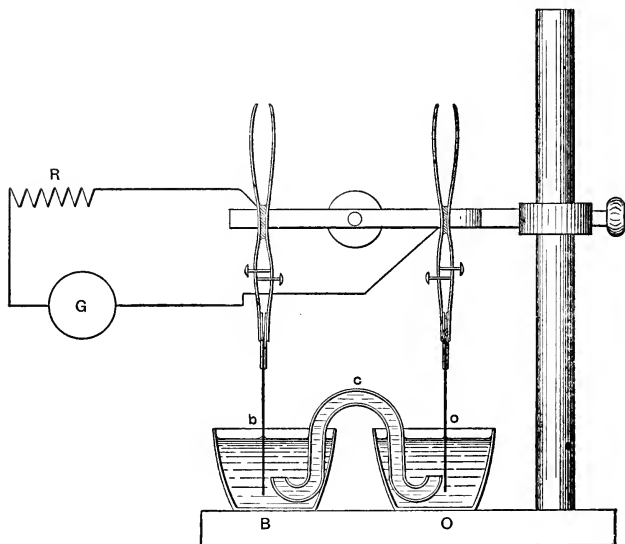
APPARATUS FOR SHOWING THE
LOCAL ELECTROLYTIC ACTION
INVOLVED IN THE
SOLUTION OF GOLD IN
AERATED CYANIDE SOLUTION
Fig. XIX.

two small porcelain cups, B and O, Fig. XIX., in which were immersed the two electrodes b and o. These were gold strips held in platinum-tipped forceps, connected in series with a reflecting galvanometer G of 3,000 ohms resistance, including that of the cell, and a resistance R of 30,000 ohms. The solution in either vessel is connected electrically by the liquid in the siphon C.

It is very difficult to prepare, and impossible to keep, a cyanide solution entirely free from oxygen, unless it is hermetic-

ally sealed. But the following method was selected as giving
an approximation to it. A liter of distilled water was boiled
under a filter-pump, and when most of the dissolved oxygen
had been removed cyanide of potassium was added, and the
boiling was continued a few minutes to drive out the air ab-
sorbed during the solution of the cyanide. A cork was pro-
vided with two tubes like those of an ordinary wash-bottle,
and after inserting the long tube below the surface, a layer of
paraffine oil was floated on to the surface to exclude the air.
The tip of the discharge-tube was kept closed by a cork when
not in use. It was easy, by blowing in through the short tube
above the surface of the oil, to discharge any required amount
of the solution as required, but of course each time this was
done a small amount of air entered the solution. After cool-
ing, the liquid was titrated and found to contain 0.62 per cent
potassium cyanide. A similar 0.621 per cent potassium cya-
nide solution was prepared and nearly saturated with oxygen.
Through the galvanometer G and the resistance R, a Clark
cell gave a deflection of 7 scale divisions. In vessel B were
placed 12 cc. of boiled 0.62 per cent potassium cyanide solu-
tion, and in O an equal volume of 0.621 per cent potassium
cyanide solution containing oxygen. On immersing the
gold strips, the strip in B became negative, that is, the posi-
tive current flowed from B through the solution to O, with an
electromotive force = +0.02 volt. When the liquid in both
B and O was covered with paraffine oil to exclude the air, the
electromotive force rose to +0.108 volt. On gently shaking
electrode *o*, the electromotive force rose to +0.185 volt, on
gently shaking B it fell to +0.08 volt (owing to absorbed
oxygen). On cutting out the 30,000 ohms resistance, leav-
ing that of the galvanometer (3,000 ohms), the deflection rose
to 6.5 scale divisions, coming back again on inserting the re-
sistance R to 0.6 scale divisions, or +0.12 volt. This grad-
ually fell to 0.2 scale division, or +0.04 volt, where it re-
mained for two hours. At the end of that time the resistance
was cut out and the deflection rose to 2.5 scale divisions, then,
on shaking, to 12 divisions, and then sank again to 2.7, where
it remained fairly steady for two hours longer. At the end of
this time, four hours in all, the electrodes were removed and

cleaned with gasoline and ether from the oil and solution, and it was found that the electrodes had lost weight as follows :

b lost 1.28 mg. o lost 1.73 mg.

The solutions contained in the vessels B and O and in the siphon C were also assayed with the following results :

B contained 1.25 milligrams, O contained 1.68 milligrams, and C contained 0.06 milligram of gold.

The total loss of the electrodes was 3.01 milligrams, and that found was 2.99 milligrams. The difference of 0.2 milligram was probably lost in the washings of the electrodes which were not saved.

This experiment, corroborated by many others, shows clearly that the positive current flows from the deoxygenated to the oxygenated cyanide, just as theory would indicate. The fact that more gold has dissolved in the oxygenated than in the deoxygenated cyanide, does not militate against the indication of the galvanometer.

The solution of the gold in the vessel O is evidently due to the well-known phenomenon of "local action." The current that flows through the siphon has to overcome a resistance of from 3,000 to 33,000 ohms, while local action can go on in the vessel O wherever an OH(—) ion comes in contact with gold and potassium cyanide. Here it forms a "short circuit," and it completes itself on the gold strip o at any point free from oxygen, without having to pass through the entire external circuit.

It might be objected that the fact that 1.73 milligrams of gold had dissolved in O as against 1.28 in B only went to prove that some oxygen had been contained in B, though less than in O, and that the solution in each had been simply in proportion to the oxygen present. But this does not account for the absolute verdict of the galvanometer, which shows that the positive current flows during the entire experiment from strip b through the solution to the strip o. The only explanation that remains is the one which I have suggested. There is no doubt that considerable local action went on in cell O. That this was the case is also evidenced by the fact that the action was more uniformly distributed over the surface of b,

while the strip *o* was not uniformly acted on, but was eaten into in a remarkable manner. These strips, and particularly some of those to be described later (with peroxide of hydrogen), were not corroded most upon the edges, where one would naturally expect it, but along vertical lines running up and down the middle of the strip. In some cases they were eaten through along these lines in such a manner that nothing remained but a thin film like gold lace. It appeared that local action started in along these lines rather than at the edges, owing to differences of potential due to the distribution of the oxygen, and that when it had once set in it was able to maintain itself.

It is probable that in all cases of the solution of gold in the aerated cyanide solutions the process, as in the above case, is one of local electrolytic action, though, as it is impossible in such a case to apply the galvanometer, it would be difficult to prove this proposition except by inference.

In all such experiments it is important to be certain that the gold strips are in the same physical state, since the existence of microscopic films or unweighable traces of occluded gas cause an appreciable difference of potential in apparently similar gold strips. This is best tested by comparing the strips in the same solution. They react similarly if they are carefully cleaned with boiling acid, and are then washed with distilled water and ignited to redness side by side in the muffle or over a bunsen flame in a small porcelain dish. But if they are heated in different parts of the same bunsen flame, they frequently show quite appreciable differences of potential due to occluded gases.

The Effect of Hydrogen Peroxide.

The peroxide of hydrogen used was Marchand's medicinal, containing 3.3 per cent of available peroxide, as determined by titration with permanganate of potassium. According to the new theory, the $H_2O_2(\pm)$ takes up from the gold strip *o*, which becomes positive, two units of negative electricity and dissociates into $2(OH)(-)$.

In the first experiment $\frac{M}{I}$-KCN solution containing the

usual amount of absorbed oxygen was used, and 10 cc. of this solution was placed both in B and O. Gold strips *b* and *o* were then placed in B and O, and the siphon was inserted. Both strips showed themselves of the same potential. The siphon was removed and 5 cc. of water was added to B and 5 cc. of hydrogen peroxide to O. On inserting the siphon and the electrodes, *b* proved to be electronegative, that is, the solution in B was electropositive by $+0.66$ volt ; in other words, the positive current flowed through the solution from *b* to *o*.

Another experiment was made with boiled water with 0.62 per cent potassium cyanide that had been kept under $\frac{1}{8}$ inch of oil for a week. B and O were each filled with 10 cc. of this solution, and the gold strips and siphon were inserted. The strips proved to be of the same potential. The siphon was then removed, and to B was added 2 cc. of distilled water, and to O 2 cc. of hydrogen peroxide. After mixing, on replacing the siphon, the voltage rose to $+0.57$ volt. That is, the positive current flowed through the solution from *b* to *o*. To exclude the air, a layer of paraffine oil about $\frac{1}{8}$ inch thick was floated over each solution before inserting the siphon.

The resistance of 30,000 ohms was then cut out, leaving only that of the galvanometer (3,000 ohms), and the needle which had previously shown a deflection of 2.6 scale divisions was thrown out of sight. (The limits of the scale used were 21 scale divisions.) After being thus short-circuited for an hour and a half, on throwing in again the 30,000 ohms resistance, the voltage of the combination showed itself to be still in the same direction, $+0.63$ volt. The 30,000 ohms were again cut out and the combination was again short-circuited over night. In the morning some bubbles of gas from the action of the peroxide had collected in the upper part of the siphon and had nearly cut off the current. But on removing and refilling the siphon the voltage still showed itself to be in the same direction, $+0.55$ volt. The resistance of 30,000 ohms was again cut out and that of the galvanometer only left in, and after five and a half hours more the electrodes were taken out, cleaned, and weighed. Total time, twenty-three hours.

The strip contained in B had lost 13.25 milligrams, while that in O had lost only 9.20 milligrams. *Evidently, in spite of the local action that has taken place in the vessel O, more gold has dissolved in the vessel B in the absence of the oxidizing agent than in O, where the oxidizing agent was present.*

In order to determine how much of the loss in B might be due to dissolved oxygen which had leaked through, or by the oil cover into the cyanide solution since it had been made, a week previously, 10 cc. of the same solution as that used in B was placed in a similar vessel, and a gold strip was immersed in it half way, and the liquid was then covered with the paraffine oil just as had been done in B and O. After nineteen and a quarter hours it had lost 4.28 milligrams. A similar strip entirely submerged below solution and oil lost, in twenty-four hours, 2.64 milligram. These experiments prove that some air had leaked through, or by, the oil cover. It had been previously proved that if a thicker layer was used, it was possible, practically, to prevent altogether the ingress of oxygen and the solution of the gold. In this case it was inconvenient to use a layer thicker than $\frac{1}{8}$ inch. But the experiment also clearly shows that the amount of gold thus dissolved by absorbed oxygen is so much less than that shown by the *b* strip, that the solution must have been caused by the electromotive forces of the combination in the manner I have explained.

The same experiment was repeated exactly as before, except that to 10 cc. of 0.62 per cent potassium cyanide in B was added 1 cc. of water and to 10 cc. in O was added 1 cc. of peroxide of hydrogen. At first the voltage was +0.652 volt, rapidly falling to +0.63 volt. After cutting out all but 3,000 ohms resistance for twenty-one hours, the voltage, on adding the 30,000 ohms, proved to be still +0.63 volt. After again cutting out the 30,000 ohms for twenty-seven hours, it still showed, on inserting it again, +0.434, rising, after resting a few minutes, to +0.456 volt. At this point, after a total of forty-seven hours, the electrodes were cleaned and weighed, and *b* was found to have lost 24.06 milligram and *o* to have lost only 13.25 milligrams. *Here, again, the positive current has moved through the solution from b to o, and more gold*

*has dissolved in the vessel containing no oxidizer than in the one
containing the oxidizer.*

In some other experiments with peroxide of hydrogen there
was more local action in O, and the *o* strip lost as much, and
in some cases even twice as much, as the *b* strip. The exact
conditions governing this local action are still under investi-
gation. *But in these cases, also, the galvanometer showed that
the positive current was still flowing through the solution from
the strip b to the strip o in contact with the cyanide containing
the oxidizer, and thence back through the gold strip o back again
to b, the place of beginning.*

The course of the negative current may be traced from the
gold strip *o* immersed in the oxygenated cyanide, to the strip
b immersed in the unoxygenated cyanide in two ways, as fol-
lows :

1. According to Ostwald[1] the reaction $O_2 + 2H_2O = 4OH$
produces $4 \times 21,000$ calories. Assuming this to be true, the
oxygen molecule O_2 forms with the water four negative hy-
droxyl ions, $4(OH)(-)$; these, assuming a negative charge
from the electrode *o*, cause that end of the gold electrode to
be positively electrified. Now these negative ions travel
through the solution, displacing at the other end of the line
four negatively electrified cyanogen ions, $4(CN)(-)$, which
give up their negative charge at the other gold electrode *b*,
and thus enable four positive gold ions, $4Au(+)$, to go into
solution there, forming with eight cyanogen ions four complex
negative ions, $4(Au(CN)_2)(-)$.

The water present may be regarded as not dissociated ap-
preciably, and the dilute solution of cyanide of potassium as
entirely so. Making these assumptions, the principal reac-
tions may be expressed as follows :

$$O_2(\pm) + 2H_2O(\pm) + 4Au(\pm) + 8K(+) + 8(CN)(-) =$$
$$8K(+) + 4OH(-) + 4(Au(CN)_2)(-).$$
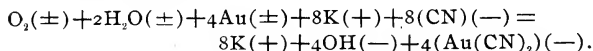
But this is equivalent to the so-called Ellsner reaction :

$$O_2 + 2H_2O + 4Au + 8KCN = 4KAu(CN)_2 + 4KOH,$$
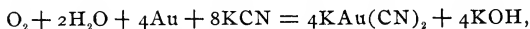
which Maclaurin[2] has proved to be quantitatively correct.

[1] "Chemische Energie," p. 956.
[2] J. Chem. Soc., **63**, 728.

2. The other view, following Traube, has been urged by Bodlaender, of the Clausthal *Bergakademie*.[1] He shows first, in agreement with Maclaurin and myself, that the reaction

$$H_2O + 2Au + 4KCN = 2KAu(CN)_2 + 2KOH + H_2,$$
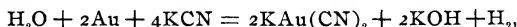
proposed by Macarthur to explain the solution of cyanide of gold in cyanide solutions, is incorrect. Next, he claims that the so-called Ellsner reaction really proceeds in two stages:

(*a*) The hydrogen, which is not formed according to Macarthur's reaction, is, in the presence of cyanide of potassium, water, gold, and oxygen, potentially nascent ; and a molecule of oxygen combines directly with 2 atoms of nascent hydrogen, forming hydrogen peroxide, while 2 atoms of gold dissolve ; thus:

$$O_2 + 2H_2O + 2Au + 4KCN = 2KAu(CN)_2 + 2KOH + H_2O_2.$$
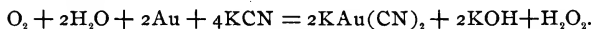
(*b*) Next, the hydrogen peroxide gradually dissociates into hydroxyl, and causes the solution of two more atoms of gold, thus :

$$H_2O_2 + 2Au + 4KCN = 2KAu(CN)_2 + 2KOH.$$
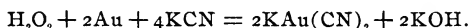
The sum of these two reactions is, of course, the same as that of the Ellsner reaction, which correctly expresses the end result.

When gold was rapidly dissolved in an aerated cyanide solution, Bodlaender was able to detect as much as 72.3 per cent of the hydrogen peroxide required by reaction (*a*) ; and, as reaction (*b*) had probably already set in, this renders this explanation extremely probable.

Expressed in terms of the ions, reactions (*a*) and (*b*) become :

(*a*) $O_2(\pm) + 2H_2O(\pm) + 2Au(\pm) + 4K(+) + 4CN(-) =$
$$4K(+) + 2Au(CN)_2(-) + 2HO(-) + H_2O_2(\pm).$$

(*b*) $H_2O_2(\pm) + 2Au(\pm) + 4K(+) + 4CN(-) =$
$$4K(+) + 2Au(CN)_2(-) + 2OH(-).$$
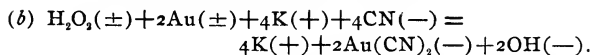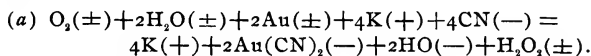
The flow of ions through the solution is the same as in the first case. On the whole, the second seems the more proba-

[1] Ztschr. angew. Chem., 1896, 583.

ble explanation, though either agrees with most of the facts.[1]

According to either of these views the new theory agrees quantitatively with the results of experiment, but offers for the first time a consistent explanation of its occurrence. *It is due to the superior electromotive force of the oxygen, or, in case they are present, to some other electronegative ions, as* $(OH)(—)$, $Cl(—)$, $Br(—)$, *etc., together with the capacity of the gold for forming complex ions with cyanogen.*

If, instead of having the two ends of the gold strip immersed in two separate cyanide solutions, the strip is immersed in the same solution containing some dissolved oxy-

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[1] While this paper was in press, a paper on "Freiwillige Oxydation" (Auto-oxidation), by Dr. Manchot, of Goettingen, has appeared, in which he has examined the oxidation of a large number of phenol derivatives, such as those used as developers in photography. One of these derivatives, oxanthranol, was particularly well adapted to give quantitative results, and he was able to prove that for every molecule of oxygen absorbed a molecule of hydrogen in the oxanthranol was oxidized, and a molecule of hydrogen peroxide was formed.

Representing the organic radical by R, and the oxanthranol by RH_2, he assumes that the reaction takes place as follows:

$$RH_2 + O_2 = R + H_2O_2.$$
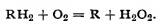
The organic radical, if unstable, is frequently still further oxidized in a second reaction by the hydrogen peroxide thus formed

It would appear that similar reactions ensue in the rusting of metals in damp air. The rusting of iron, zinc, etc., is worthy of thorough study in the light of the new ideas.

It would seem that the modern electrochemical views necessitate a return, in part at least, to the ideas of Berzelius and Schoenbein. They supposed that the same element was at times positively, and at other times negatively, electrified. This appears to be a consequence of the new view also. For if we regard the oxygen molecule $O_2(\pm)$ as electrically neutral, this can only be the case when one of its atoms has a double positive and the other an equal negative charge. By the attraction of these charges the molecule may be regarded as being held together. Its real composition then would be $O(— —) + O(+ +)$. On the other hand, two atoms of oxygen in the elemental state would be similarly electrified with negative electricity, thus: $O(— —)$, $O(—-)$, and would consequently repel each other. Hence, to change an oxygen molecule into two oxygen atoms would require four units of negative electricity.

On the other hand, the hydrogen molecule would be composed as follows: $H(+)+H(—)$; and to change it into two hydrogen atoms $H(+)$ and $H(+)$ would require two units of positive electricity.

It would also seem necessary to assume that there is an inherent tendency in the oxygen molecule (due, perhaps, to some peculiarity of shape or volume) to assume negative, and in the hydrogen molecule to assume positive electricity in dissociating.

It would also appear as if a different result ought to be produced when neutral hydrogen molecules combine with a neutral oxygen molecule, from that which results from the combination of positively electrified hydrogen atoms with a neutral oxygen molecule. This may be the key to the formation of water in the one case and hydrogen peroxide in the other.

gen, the same electrolytic action can still go on as a case fo "local action" for the couple

$$\frac{\text{Au} : \text{KCN}}{(\text{OH}) : \text{Au}}$$
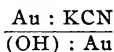
is still possible if we regard the gold to be short-circuited on itself, and the explanation given above still applies.

When I began this investigation, in 1896, I marked out for myself a much wider range of investigation than here outlined, and the course of its partial execution has suggested many other interesting questions, some of which are still under investigation, but the constant and pressing interruptions of routine work have made it impossible to carry the work further at the present time.

IV. Conclusions.

Whatever may be the nature of the objections that may be raised against the final acceptance of the modern electrolytic theory in its present form, it will, I think, be conceded that the following conclusions may be fairly drawn from the foregoing :

1. That the new electrolytic theory explains in a remarkably complete manner the reason for the departure of metals immersed in cyanide solutions from the sequence of electromotive force which they present in acid solutions.

2. That it is the only theory ever presented that gives any clue to the remarkable aberration of cyanide solutions from all the usual chemical analogies.

3. That it explains in an entirely adequate manner the reason for the reactions that go on when gold, silver, and other metals are dissolved and precipitated from cyanide solutions.

4. That the determination of the electromotive force of the metals in cyanide solutions, under different conditions, offers a means of research that is likely to be of great practical utility in determining the direction and intensity of chemical reactions, under fixed conditions, or in following them under changing conditions, just as they occur.

5. That the differences of electromotive force of metals in dilute cyanide solutions do not give much support to the so-

called "selective affinity of dilute cyanide solutions for gold," the only common metal that shows any indication of such favorable action being copper.

6. It is probable that, in the absence of external electromotive forces, an aerated cyanide solution less than $\dfrac{M}{10,000}$, or 0.00065 per cent, is without action on metallic gold.

7. That for all practical purposes, an aerated cyanide solution of less than 0.001 per cent, is without action on metallic gold.

This study has led apparently far afield from the practical side of the cyanide process; yet I hope that it may be of service in at least calling attention to the work of others who have toiled for many years in attempting to clear up some of the most subtle questions that have ever taxed the human mind, for I am firmly convinced that, in the long run, such work is always of the greatest practical service. In these days, the words of Ostwald have certainly come true:

" The science of to-day is the practice of to-morrow."

REVIEWS.

THE EXPERIMENTAL STUDY OF GASES. An account of the experimental methods involved in the determination of the properties of gases and of the more important researches connected with the subject. By MORRIS W. TRAVERS, D.Sc. Macmillan & Co. 1901.

We are but just beginning to realize the existence of matter devoid of chemical properties, which seems to have been predestined from the beginning of things never to enter into combination. These elements, for elements they seem to be, which went into the "discard," so to speak, during the process of cosmical evolution, have either remained free in the earth's atmosphere, or else have been locked up as mechanical inclusions in certain minerals.

Those which have been discovered up to the present time are all gaseous, but there seems to be no reason why we may not suspect the existence of inert substances which are either solid or liquid under ordinary conditions. Possibly the minute traces of insoluble residue which are left over in certain mineral analyses, and described as "probably silicon" or "doubtless rhodium" will bear looking into. It was the small insoluble residue in a certain gas reaction that furnished the

first clue to the existence of this interesting class of elements. The separation and purification of substances of this nature must clearly be accomplished by physical means, and the two physical processes generally made use of for the separation of dissimilar substances, are crystallization and fractional distillation. Fortunately the great advances which have been made during the last ten years in the methods of getting extremely low temperatures, make the application to gases of the process of fractional distillation, and even crystallization, almost as simple as it is in the case of liquids. Mr. Travers has given us a very satisfactory handbook on the subject of the experimental study of gases, which will be found extremely useful to every chemist and physicist. It is profusely illustrated, and an unusually large amount of space is given to manipulation, a circumstance which will make every experimenter grateful to the author.

Nearly 100 pages, at the start, are devoted to mercury pumps, stop-cocks, various forms of apparatus used in storing, transferring and measuring gases, methods of preparing pure gases, and the devices necessary to the handling of small amounts of rare gases to the best advantage.

The chapter on the measurement of volume, and the one following it on gas analysis, will be found of especial interest to chemists. The author recommends the use of the siphon burette unless a large number of analyses are to be made. With this piece of apparatus, which any one with a rudimentary knowledge of glass-blowing can construct for himself, the complete analysis can be made, the reagents being kept in ordinary bottles instead of in the somewhat complicated pipettes described by Hempel and others. The method seems to be especially adapted to laboratories provided with a limited equipment.

In brief, it consists in the introduction into a tube filled with mercury and inverted over a jar of the same fluid, of a small quantity of the gas-absorbing reagent. The gas is then allowed to bubble up into the tube from the graduated siphon burette. After the absorption the residue is drawn back into the pipette and its volume recorded. The same process is then repeated with the other reagents, the final explosion being made in the same instrument by means of eudiometer electrodes sealed into the top of the graduated tube. The simplicity of the method is its strong recommendation, although, as the author says, the Oettel pipettes will probably be found more convenient in the case of commercial analyses.

Following this we have an interesting account of the inert gases helium, argon, neon, krypton, and xenon, and the

methods by which they were isolated. This subject is treated very explicitly; if the experimenter wishes to collect a small amount of argon to fill a vacuum-tube, or prepare a large quantity for the investigation of its physical properties, the best method for each case is given.

The author next takes up the determination of gas density and the relations between temperature pressure and volume. Following this comes the subject of the liquefaction of gases, in which the developments are traced from Faraday's bent tube to the regenerative machines of Linde and Hampson for the liquefaction of air. This chapter concludes with a very complete description of the apparatus used by the author for the liquefaction of hydrogen, and of the precautions which must be taken in its use. A chapter follows on the manipulation of liquid gases, their fractional distillation, and their use in the maintaining of constant low temperatures.

The author throws out frequent suggestions to those engaged upon research work, pointing out many of the gaps in our knowledge which require filling, such, for example, as the effect of pressure on the composition of the distillate passing over at a definite temperature. This question has been investigated in the case of water and certain organic fluids, but practically nothing is known of the behavior of mixtures of liquefied gases. This is a question of vital importance in the separation of gases by physical processes.

The last part of the book is devoted to the determinations of vapor-pressure and the critical constants, the specific heat of gases, and the phenomena of effusion, transpiration, and diffusion, the closing chapter dealing with the subject of spectrum analysis, with instructions for the construction, filling, and use of vacuum tubes, which will be found helpful. If one has but a cubic centimeter of a pure gas and will fill a vacuum tube with it and then recover all but the minute trace left in the exhausted tube, without contaminating it with impurities in the meantime, it is important to know beforehand exactly how to proceed, and exactly what precautions to take.

The book contains a vast amount of information and is admirably adapted to the requirements of students, both as a text-book and as a guide to work in the laboratory whether elementary or advanced.

Sufficient space is given to theory and experiment to make it interesting reading, while the very large amount of information regarding manipulation makes it invaluable in the laboratory as a reference book.

Mention should be made too of the admirably executed diagrams. We none of us ever quite get over the early contracted

habit of liking to look at the pictures, and the pictures in Mr. Travers' book certainly invite the reader to take up the study of gases for the mere pleasure of making and using the apparatus, if for nothing else. R. W. WOOD.

THE ELEMENTS OF PHYSICAL CHEMISTRY. By HARRY C. JONES. New York : The Macmillan Company. 1902. pp. 565 + vii. Price, $4.00.

The following extracts from the preface of this book will serve to introduce it to chemists :

" It has been the aim of the author to deal with the whole subject of physical chemistry in an elementary manner. The rapidly increasing desire, on the part of students of chemistry and physics, to know more of physical chemistry is manifesting itself in every direction. It is with the object of helping such students in the later stages of their college work and in the earlier part of their university career that this work has been prepared."

" In reference to the contents of that portion of the work which deals with the newer physical chemistry, a few words should be added in this connection. The new physical chemistry really begins with the chapter on solutions, and this is one of the most important chapters. The discovery of the relations between dilute solutions and gases has placed the subject of solutions at the very foundations of the new developments in physical chemistry."

" Electrochemistry, on the other hand, is of the very greatest importance. In no chapter of physical chemistry have greater advances been made in recent time, and nowhere do we find experimental work of greater value.

"The study of chemical dynamics and statistics has been very much to the front ever since the recognition of the importance of the law of mass action. It will be observed that reaction velocities and equilibrium in chemical reactions have been dealt with from the standpoint of this law. This appeals to the author as being the most exact and by far the simplest method of treating these problems. The phase rule, however, is considered at sufficient length, and applied, it is hoped, to a sufficient number of cases to make clear this important generalization.

"An attempt has been made to prepare a balanced work. The danger of treating certain subjects too fully and of following certain deductions beyond the scope of the remainder of the book has been felt, and an earnest endeavor has been made to avoid this defect."

" Little need be said at this date in reference to the importance of the whole subject of physical chemistry. It has already extended into nearly every field of chemical science,

contributing largely to the interpretation of phenomena hitherto not understood. It has thrown light on so many problems in chemistry that it has now become an integral part of that science. And it is recognized that no chemist to-day, scientific or technical, can omit physical chemistry without losing an essential part of his training.''

SAMMLUNG CHEMISCHER UND CHEMISCH-TECHNISCHER VORTRÄGE. Herausgegeben von PROFESSOR DR. FELIX B. AHRENS. VI Band; 12 Heft. Ueber feste Lösungen, von Dr. Guiseppe Bruni, Privatdocent an der Universität Bologna. Deutsch von Dr. E. E. Basch, Wien. Mit 4 Abbildungen. 1901. pp. 55. Verlag von Ferdinand Enke, Stuttgart.

This monograph begins with a discussion of the origin of the conception of solid solutions, and then takes up the methods by which solid solutions can be formed. A very brief section is devoted to the state of molecular aggregation of substances in the solid condition, and the phase rule is then applied at length to the subject of solid solutions.

The second portion of the monograph is devoted to the relations between the chemical constitution of substances which can form solid solutions with one another. This comprises both inorganic and organic compounds, and discusses the beautiful investigations of Piccini, Garelli, Ciamician, Ferratini, and others.

It is to be regretted that one of the most important investigations on solid solutions has not found its way into this monograph. Küster has shown how it is possible to determine the molecular weights of pure solids by means of solid solutions, and has furnished us with the only method available for determining the molecular weights of solids. This is indeed the most important scientific application of the ideas worked out by van 't Hoff concerning the existence and nature of solid solutions.

The author has increased the value of his work by giving reference to the literature of his subject. H. C. J.

PHYSIKALISCHE CHEMIE FÜR ANFÄNGER. Von DR. CH. M. VAN DEVENTER. Mit einem Vorwort von PROF. DR. J. H. VAN 'T HOFF. Zweite Auflage, besorgt von DR. ERNST COHEN. Amsterdam : S. L. Van Looy ; Leipzig: Wilhelm Engelmann. 1901. pp. 168.

The appearance of the first edition of this book has already been noticed in this Journal. (Vol. 19, 916.) The translation into English was subsequently reviewed (Vol. 21, 277), and it now only remains to call attention to the fact that the second German edition has appeared. H. C. J.

AMERICAN

CHEMICAL JOURNAL

XX.—CAMPHORIC ACID.

[ELEVENTH PAPER.]

CONFIRMATION OF BREDT'S FORMULA ; SOME DERIVATIVES OF INACTIVE CAMPHORIC ACID.

BY WILLIAM A. NOYES AND AUSTIN M. PATTERSON.

Some time ago one of us[1] prepared synthetically the 2.3,3-trimethylcyclopentanone and proved it to be identical with a ketone prepared from dihydro-β-campholytic acid.   This was the first synthesis of a cyclic derivative of camphor, and confirmed the view previously expressed by Blanc as to the structure of β-campholytic acid.   In the same connection, the opinion was expressed[2] that the relation between α-campholytic acid ("cistranscampholytic acid") and β-campholytic acid ("ciscampholytic acid") is one of stereoisomerism. Later, further evidence pointing in the same direction has been furnished.[3]   Results obtained, however, by Kershbaum

[1] This JOURNAL, **23**, 130.

[2] *Loc. cit.*, p. 134.

[3] Noyes and Phillips : This JOURNAL. **24**, 285; Noyes and Blanchard : *Ibid.*, **26**, 283.

27–27

and Tigges,[1] by Blanc,[2] and by Lapworth[3] are quite inconsistent with this conclusion and point to the following relation between the two acids:

$$
\begin{array}{c}
CH_3 \\
\diagdown \\
C{-}CH{-}CO_2H \\
CH_3\diagup \quad | \\
CH_2 \\
| \\
CH_3{-}C{=}CH
\end{array}
\qquad
\begin{array}{c}
CH_3{-}C{=}C{-}CO_2H \\
\phantom{CH_3{-}C{=}C}| \\
\phantom{CH_3{-}C{=}C}CH_2 \\
CH_3 \quad | \\
\diagdown \\
C{-}CH_2 \\
CH_3\diagup
\end{array}
$$
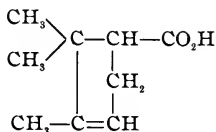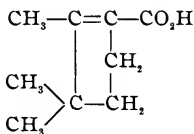
α-Campholytic acid. β-Campholytic acid.

According to these formulas, the transformation of the α- to the β-acid is accompanied by a transfer of a methyl group from the α- to the β-position, as well as by a shifting of the double union. A new, and apparently a very decisive, proof that such a transfer occurs has now been obtained.

In the last paper[4] the preparation of dihydro-α-campholytic acid was described. This acid has now been carried through the same series of transformations which were some time ago applied to the dihydro-β-campholytic acid[5] ("dihydrociscampholytic acid" or "dihydroisolauronolic acid"). These transformations are:

$$
C_8H_{15}CO_2H \;\longrightarrow\; C_8H_{14}{\diagup}^{CO_2C_2H_5}_{\diagdown Br} \;\longrightarrow\; C_8H_{14}{\diagup}^{CO_2H}_{\diagdown OH} \;\longrightarrow
$$

$$
C_8H_{14}O \;\longrightarrow\; C_8H_{14}{=}NOH.
$$
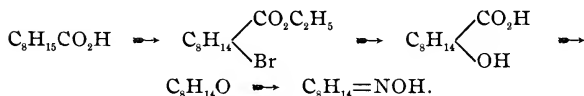
It seems unnecessary to repeat the details of the various steps as they were all carried out essentially as with the isomeric acid. The shaking of the ester of the α-bromdihydrocampholytic acid with an aqueous solution of barium hydroxide was continued for ten days at a temperature of 40° to 50°, and the decomposition was then still far from complete. The saponification and decomposition were finally completed by boiling the mixture with an upright condenser for some

[1] *Ber. d. chem. Ges.*, **33**, 2938.
[2] *Compt. rend.*, **131**, 803.
[3] *J. Chem. Soc.* (London), **79**, 1284.
[4] This JOURNAL, **26**, 288.
[5] *Ibid.*, **22**, 262.

hours. The mixture of the hydroxy acid and the Δ^5-campholytic acid[1] obtained, was separated by neutralizing with ammonia and distilling with steam. The ammonium salt of the Δ^5-acid dissociates readily and passes over, while the larger portion of the hydroxy acid remains behind. The latter was obtained only as an oil. It forms a difficultly soluble calcium salt which was analyzed. The salt dried at 110° gave 10.53 per cent of calcium. Theory requires 10.46 per cent. The amount of the hydroxy acid obtained was very much smaller than in working with the isomeric acid, and only a few centigrams of the oxime of the ketone were finally secured. It was possible to crystallize the oxime from ligroin, however, and to secure what seemed to be a quite perfect purification.

The new oxime, which must be that of 2,2.3-trimethylcyclopentanone, crystallizes in plates which melt at 104°, curiously enough, at exactly the same temperature as does the oxime of the 2.3,3-trimethylcyclopentanone mentioned above. The latter, however, crystallizes in needles instead of plates, and a mixture of the two melts at 80° or below. There can, therefore, be no doubt that the two oximes, and hence the two ketones, are different.

If the two campholytic acids were stereomeric compounds, as one of us formerly supposed, the ketones prepared from the two dihydro acids would each have the structure

$$CH_3-CH-CO$$
$$| \qquad |$$
$$\qquad CH_2$$
$$CH_3 \diagdown \qquad | \quad .$$
$$\qquad C-CH_2$$
$$CH_3 \diagup$$
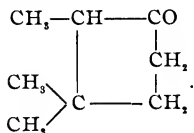
A ketone of this structure can exist in two optically active and in an inactive form, but there can be no "cis" and "trans" isomerism. Since the campholytic acids used in each case were inactive, the resulting ketones and oximes must also be inactive, and the fact that they are different establishes for them a different structure. The only rational explanation of such a result seems to be that of the wandering of a methyl

[1] This Journal, **26**, 291.

group in the transformation of either campholytic acid into the other. This leads to the following formulas for the new ketone and for α-campholytic acid :

2,3-Trimethylcyclopentanone.   α-Campholytic acid.
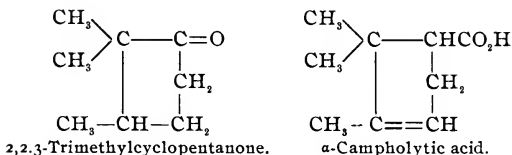
This result furnishes, as has been stated, a new and very positive confirmation of Bredt's formula.

Before leaving this part of the subject it seems worth while to point out that the work done with the campholytic acids has brought out certain facts which cannot be readily explained by the current stereochemical theories and which seem, in part, at variance with those theories.

First, the addition of hydrobromic acid to α-campholytic acid should give rise to two configurations according as the acid adds itself on the one side or the other of the plane of the ring. In one of these the bromine and carboxyl would be "cis," in the other "trans." But it has been shown in a previous paper[1] that a single configuration is almost or quite exclusively formed. This must be the "cis" form, if camphoric acid has the "cis" configuration, as is usually supposed. Second, the transformations of α-campholytic acid to β-campholytic acid, and *vice versa*, are supposed to occur through the following steps :

α-Campholytic acid.   Hydrobromide of α-campholytic acid.

[1] This JOURNAL, **24**, 291.

Hydrobromide of β-cam-
pholytic acid.
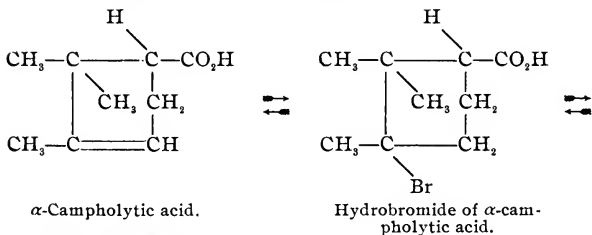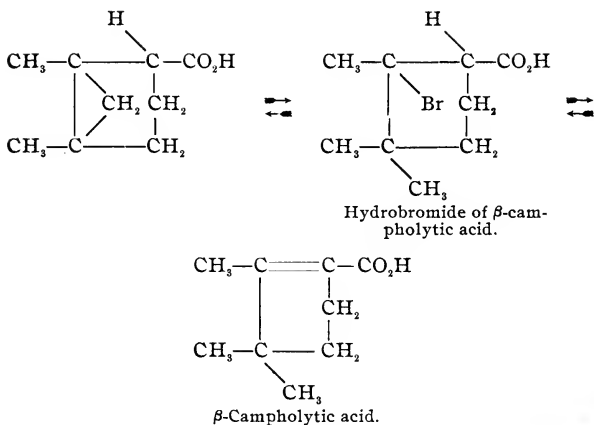
β-Campholytic acid.

An examination of these formulas shows that the bromine and carboxyl of the hydrobromide of β-campholytic acid are *cis* when it is derived in this manner from α-campholytic acid, while they should be *trans* if derived directly from the β-campholytic acid. Assuming camphor and camphoric acid to have the *cis* configuration, no consistent explanation of the facts along such lines seems possible.

While the stereochemical theories have been very successful in explaining optical isomerism and in predicting the number of possible isomers, they occasionally break down completely when the attempt is made to apply them logically to questions of the above description.

The work here described was already practically complete when an article by Blanc[1] appeared in which he describes the preparation of a ketone through the following series of compounds:

$C_6H_{13}CH_2CO_2H \rightarrowtail C_8H_{15}CH_2CO_2H \rightarrowtail C_8H_{15}CHBrCO_2H \rightarrowtail$
α-Campholenic
acid.

$$C_8H_{14}{=}CHCO_2H \rightarrowtail C_9H_{14}O.$$
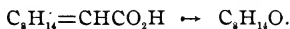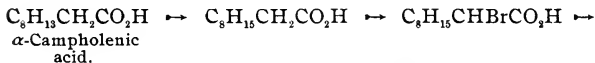
[1] Bull. Soc. Chim., **27,** 71.

The oxime of this ketone melts at 107° to 108° and is different from the oxime of the ketone from dihydro-β-campholytic acid, and on this fact Blanc bases the conclusion that it must have a different structure. But the α-campholenic acid is optically active, and if that activity continues through the series the ketone obtained by Blanc might be, so far as the evidence goes, simply one of the active components of the racemic ketone obtained from dihydro-β-campholytic acid. The proof is, therefore, inconclusive, while the evidence given here is based on work with racemic compounds throughout, and leads to a conclusion which seems to be very positive. Except on the supposition that Blanc's ketone was in reality active, it seems difficult to reconcile the fact that his oxime melts at a temperature 3° to 4° higher than ours.[1]

In previous papers the opinion has been expressed that α-campholytic acid has a structure in which there is no asymmetric carbon atom and a stereomeric structure which would account for its optical activity was proposed.[2] This formula is, of course, no longer tenable.

Derivatives of Inactive Camphor.

A short time ago the attention of one of us was called to the fact that the Ampère Electro-Chemical Company, of New York, has been preparing to manufacture artificial camphor. The details of the process are not yet public, but the starting-point is, of course, turpentine. Through the kindness of the company we have been furnished with about 400 grams of their product. It is genuine *inactive* camphor. It melts at 176° and is optically inactive. On oxidation with nitric acid[3] it conducts itself in the same manner as ordinary camphor and yields *i*-camphoric acid melting at 204°, and this by

---

[1] Since writing the above we have received a sample of this oxime, which Dr. Blanc has very kindly sent us. We find that it melts about 3° higher than our oxime, but that a mixture of the two melts partially at the melting-point of our oxime, 103° to 104°. We are not aware that any one has recorded observations as to the melting-point of the mixture of a racemic compound with one of its active components, but it would seem that these observations agree best with the supposition that Dr. Blanc's oxime is active while ours is racemic. It is also possible that ours is not quite pure. Dr. Blanc writes us that he will repeat the preparation of his ketone, starting with inactive camphor.

[2] This JOURNAL, **24**, 287.

[3] *Ibid.*, **16**, 501.

treatment with acetic anhydride and acetyl chloride[1] gave camphoric anhydride melting at 225°. The nitric acid mother-liquors, after the oxidation, gave, on evaporation to dryness, solution of the residue in ammonia, adding barium chloride and warming, a copious crystalline precipitate, evidently barium camphoronate.[2]

In the last paper[3] an account of an inactive dihydrohydroxy-campholytic acid and of its separation into the active components was given. On that work, chiefly, was based the view that the racemic α-campholytic acid used as the starting-point for the present study differs from the ordinary α-campholytic acid only in its optical inactivity. Since experience has shown that molecular rearrangements are especially frequent with this class of compounds, it is important to check every point as far as possible by independent observations which may lead to the same conclusion. In the present case it was, therefore, interesting to prepare the i-dihydrohydroxycampholytic acid directly from the i-camphor. This has been done.

Fifty grams of the i-camphoric anhydride were suspended in 100 cc. of alcohol, ammonia gas was passed in till solution was complete and the resulting solution was distilled slowly, while a slow current of ammonia was continued till the boiling-point of the imide was reached. The resulting imide[4] was not purified but was dissolved in 140 cc. of a 15 per cent solution of sodium hydroxide and the solution was heated on the water-bath for two hours. On cooling and standing for a short time the sodium salt of the β-camphoramidic acid, which had been formed, separated. The separation can be hastened by adding a little β-camphoramidic acid from a previous preparation, if that is available. The salt was filtered off, washed with a very little 10 per cent sodium hydroxide, dissolved in water, and the acid precipitated with hydrochloric acid. The acid can be most easily purified by dissolving it in a small amount of concentrated hydrochloric acid, filtering on

[1] *Loc. cit.*, p. 502.
[2] The work thus far was done by Mr. R. C. Warren.
[3] This JOURNAL, **26**, 286.
[4] *Ibid.*, **16**, 502.

asbestos, and precipitating by dilution with 2 or 3 volumes of water.

i-β-Camphoramidic acid, $C_8H_{14}\begin{smallmatrix}CO_2H\\CONH_2\end{smallmatrix}$, prepared as described, crystallizes in needles which melt at 178°. The active isomer melts at 182° to 183°.[1] 0.2011 gram of the acid required for its neutralization 10.28 cc. of N/10 potassium hydroxide. Theory requires 10.11 cc.

i-Dihydroaminocampholytic acid, $C_8H_{14}\begin{smallmatrix}CO_2H\\NH_2\end{smallmatrix}$, was prepared by exactly the same process used in the preparation of the active isomer.[2] It crystallizes in leaflets and so closely resembles the active body as scarcely to require a new description. The *chloroplatinate* is easily soluble. The *anhydride*, $C_8H_{14}\begin{smallmatrix}CO\\|\\NH\end{smallmatrix}$, melts at 188°, the same temperature as the melting-point of the anhydride of the active acid.[3]

i-Dihydrohydroxycampholytic Acid.—When the amino acid is treated with 0.5 molecule of sulphuric acid and 1 molecule of sodium nitrite it decomposes in a manner exactly similar to that of the decomposition of the active body,[4] yielding *i*-dihydrohydroxycampholytic acid and racemic α-campholytic acid. The hydroxy acid melted at 173°. The melting-point was given in our last paper as 176°, but a specimen of the old acid was now found to melt at 173°, and a mixture of the two acids melted at exactly the same temperature. The identity of the two is therefore beyond question. The melting-point here given was corrected by checking the thermometer with boiling aniline (183°.7).

The *i-α-campholytic acid* was obtained in small amount as a liquid. Its amide melted at 99°, the same temperature found for the melting-point of the amide of the acid prepared from β-campholytic acid, as described in our last paper, and a

[1] This JOURNAL, **16**, 310.
[2] *Ibid.*, **16**, 503.
[3] *Ibid.*, **16**, 504.
[4] *Ibid.*, **17**, 424.

mixture of the two amides melted at the same temperature.[1]
Warming with dilute sulphuric acid (1 : 1) converts the acid
into β-campholytic acid.

TERRE HAUTE, IND.,
April 2, 1902.

THE LOWERING OF THE FREEZING-POINT OF WATER PRODUCED BY CONCENTRATED SOLUTIONS OF CERTAIN ELECTRO-LYTES, AND THE CONDUC-TIVITY OF SUCH SOLUTIONS.

BY HARRY C. JONES AND FREDERICK H. GETMAN.

We had hoped to carry this investigation much farther be-
fore publishing the results obtained, but a paper which has
just appeared, by W. Biltz,[2] bearing upon the same subject,
makes this preliminary publication necessary. Since the
minimum in the molecular lowering of the freezing-point of
water, produced by a large number of electrolytes, was dis-
covered for most of these substances in this laboratory, and
systematically studied for the first time by Jones and Cham-
bers,[3] it seemed reasonable to expect that we would be given
a fair amount of time to extend our investigations into this
field which we had entered. This seemed all the more prob-
able in that Jones and Chambers[4] stated at the close of the
first investigation of this problem that " we propose to extend
this investigation to a much larger number of hygroscopic
substances, to ascertain whether there is any relation between
this property and abnormal freezing-point lowerings, such as
those recorded in this paper."

And Chambers and Frazer,[5] working with Jones, concluded
their paper as follows : " It seems to us quite possible that
work of the kind here described may help, if only a little,

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[1] Blanc gives the melting-point as 103°. Our amide is evidently not quite pure, but when mixed with a sample of Dr. Blanc's amide, which he kindly sent us, the mixture melted at 101°. The two are, therefore, identical.

[2] Ztschr. phys. Chem., **40,** 185 (1902).

[3] This JOURNAL, **23,** 89 (1900).

[4] *Ibid.,* p. 105.

[5] *Ibid.,* **23,** 520 (1900).

towards the understanding of concentrated solutions, and we may thus be able to find out why it is that the laws which obtain for dilute solutions do not hold in the more concentrated. It is with this hope in mind that further work along the above line will be done.''

The investigation, of which a preliminary account is here recorded, has for its object the study of a large number of electrolytes in water, to determine whether the minimum in the molecular lowering of the freezing-point was a general phenomenon, or whether it was manifested only by certain substances. We also desired to measure the freezing-point lowering produced by solutions of electrolytes of such great concentration that the ordinary Beckmann thermometer could not be employed. We, therefore, had two large Beckmann thermometers constructed. One of these had a range of 12° and was divided into fiftieths of a degree, and the other had a range of 25° and was divided into twentieths of a degree. The former was used for the more dilute solutions, the latter for the more concentrated. The apparatus employed was essentially that devised by Beckmann. The freezing-mixtures used in this work were sodium chloride and ice, and calcium chloride and ice. Several acids, one base, and a number of salts have been studied, as will be seen from the following results.

Column I. contains the concentrations of the solutions in terms of gram-molecular normal; II. is the observed lowering of the freezing-point of water; III., the correction due to the separation of ice; IV., the corrected lowering of the freezing-point; and V., the molecular lowering of the freezing-point.

In some cases two, in other cases three, determinations of the freezing-point of a solution were made. The mean of the several values is given in every case.

Hydrochloric Acid.
HCl (36.46).

I.	II.	III.	IV.	V.
1.0	4.130	0.012	4.118	4.118
1.0	4.150	0.025	4.125	4.125
			Mean,	4.122
1.5	6.690	0.066	6.620	4.413
1.5	6.750	0.108	6.640	4.427
			Mean,	4.420
2.0	10.160	0.304	9.860	4.928
2.0	10.275	0.257	10.018	5.009
			Mean,	4.969
2.5	13.550	....	13.550	5.420
2.5	13.470	0.055	13.420	5.370
			Mean,	5.400
3.0	18.100	0.004	18.096	6.030

Nitric Acid.
HNO_3 (63.05).

I.	II.	III.	IV.	V.
0.25	0.910	0.038	0.872	3.488
0.25	0.920	0.039	0.881	3.524
0.25	0.900	0.027	0.873	3.492
			Mean,	3.501
0.5	1.840	0.025	1.815	3.630
0.5	1.840	0.011	1.820	3.640
0.5	1.820	0.024	1.796	3.592
			Mean,	3.621
1.0	3.850	0.016	3.834	3.834
1.0	3.840	0.063	3.777	3.777
1.0	3.860	0.082	3.778	3.778
			Mean,	3.796
1.5	5.980	0.043	5.937	3.958
1.5	5.980	0.043	5.937	3.958
1.5	5.980	0.040	5.940	3.960
			Mean,	3.959

Nitric Acid (*Continued*).

I.	II.	III.	IV.	V.
2.0	8.400	0.015	8.385	4.193
2.0	8.450	0.105	8.345	4.173
2.0	8.525	0.213	8.312	4.156
			Mean,	4.174
2.5	11.125	0.060	11.065	4.426
2.5	11.125	0.078	11.047	4.418
2.5	11.125	0.099	11.026	4.410
			Mean,	4.418
3.0	13.950	0.279	13.671	4.557
3.0	14.150	0.071	14.079	4.693
3.0	14.075	0.099	13.976	4.659
			Mean,	4.603

Sulphuric Acid.
H_2SO_4 (98.08).

I.	II.	III.	IV.	V.
0.1	0.415	0.017	0.398	3.980
0.1	0.412	0.016	0.396	3.960
0.1	0.411	0.015	0.396	3.960
			Mean,	3.970
0.2	0.820	0.003	0.817	4.090
0.2	0.820	0.003	0.817	4.090
0.2	0.820	0.002	0.818	4.090
			Mean,	4.090
0.3	1.190	0.022	1.168	3.890
0.3	1.180	0.005	1.175	3.920
0.3	1.200	0.024	1.176	3.920
			Mean,	3.910
0.4	1.600	0.020	1.580	3.950
0.4	1.610	0.022	1.588	3.970
0.4	1.640	0.030	1.610	4.020
			Mean,	3.980
0.5	2.040	....	2.040	4.080
0.5	2.040	....	2.040	4.080
0.5	2.040	0.023	2.017	4.030
			Mean,	4.060

Sulphuric Acid (Continued).

I.	II.	III.	IV.	V.
1.0	4.210	0.019	4.191	4.191
1.0	4.200	0.006	4.194	4.194
1.0	4.200	0.016	4.184	4.184
			Mean,	4.190
1.5	7.450	0.008	7.442	4.961
1.5	7.450	0.006	7.444	4.963
1.5	7.450	0.008	7.442	4.961
			Mean,	4.962
2.0	11.325	0.005	11.320	5.660
2.0	11.300	0.005	11.295	5.648
2.0	11.275	0.002	11.273	5.637
			Mean,	5.648
2.5	16.275	....	16.275	6.510

Potassium Hydroxide.

KOH (56).

I.	II.	III.	IV.	V.
0.2	0.730	0.005	0.725	3.630
0.2	0.723	0.009	0.714	3.570
0.2	0.728	0.009	0.719	3.600
			Mean,	3.600
0.5	1.820	0.022	1.798	3.596
0.5	1.810	0.002	1.808	3.616
0.5	1.810	0.002	1.808	3.616
			Mean,	3.609
1.0	3.920	0.045	3.875	3.875
1.0	3.940	0.031	3.909	3.909
1.0	3.920	0.034	3.886	3.886
			Mean,	3.890
1.5	5.975	0.013	5.962	3.975
1.5	5.975	0.010	5.965	3.977
1.5	5.975	0.010	5.965	3.977
			Mean,	3.976

Potassium Hydroxide (Continued).

I.	II.	III.	IV.	V.
2.0	8.475	0.007	8.468	4.234
2.0	8.450	0.003	8.447	4.224
2.0	8.550	0.009	8.541	4.270
			Mean,	4.243
2.5	11.375	0.009	11.366	4.546
2.5	11.300	0.005	11.295	4.518
2.5	11.250	0.004	11.246	4.498
			Mean,	4.521

Calcium Chloride.

$CaCl_2$ (110.8).

I.	II.	III.	IV.	V.
0.5	2.740	0.002	2.738	5.476
0.5	2.730	0.002	2.728	5.456
0.5	2.750	0.007	2.743	5.486
			Mean,	5.473
1.0	6.350	0.008	6.342	6.342
1.0	6.350	0.002	6.348	6.348
1.0	6.330	0.006	6.324	6.324
			Mean,	6.338
1.5	11.300	0.004	11.296	7.531
1.5	11.325	0.005	11.320	7.547
1.5	11.300	0.004	11.296	7.531
			Mean,	7.536
2.0	17.975	0.002	17.973	8.987
2.0	17.875	0.008	17.867	8.934
2.0	17.875	0.008	17.867	8.934
			Mean,	8.952

Strontium Chloride.

$SrCl_2$ (158.5).

I.	II.	III.	IV.	V.
0.5	2.620	0.005	2.615	5.230
0.5	2.630	0.008	2.622	5.244
0.5	2.610	0.005	2.605	5.210
			Mean,	5.228

Strontium Chloride (Continued).

I.	II.	III.	IV.	V.
1.0	6.060	0.017	6.043	6.043
1.0	5.960	....	5.960	5.960
1.0	6.010	0.003	6.007	6.007
			Mean,	6.003
1.5	10.825	0.005	10.820	7.213
1.5	10.725	....	10.725	7.150
1.5	10.725	....	10.725	7.150
			Mean,	7.171
2.0	16.450	0.005	16.445	8.223
2.0	16.425	0.003	16.422	8.211
2.0	16.425	0.003	16.422	8.211
			Mean,	8.215

Barium Chloride.
$BaCl_2$ (208.3).

I.	II.	III.	IV.	V.
0.25	1.230	0.001	1.229	4.916
0.25	1.270	0.046	1.224	4.900
0.25	1.230	0.001	1.229	4.916
			Mean,	4.911
0.50	2.550	0.024	2.526	5.052
0.50	2.500	0.007	2.493	4.986
0.50	2.550	0.030	2.520	5.040
			Mean,	5.023
0.75	4.010	0.003	4.007	5.343
0.75	3.860	0.005	3.855	5.140
0.75	3.860	0.001	3.859	5.145
			Mean,	5.209

Sodium Nitrate.
$NaNO_3$ (85.09).

I.	II.	III.	IV.	V.
0.05	0.200	0.001	0.199	3.980
0.05	0.205	0.002	0.203	4.060
0.05	0.195	0.002	0.193	3.860
			Mean,	3.967

Sodium Nitrate (Continued).

I.	II.	III.	IV.	V.
0.1	0.370	....	0.370	3.700
0.1	0.370	0.002	0.368	3.680
0.1	0.355	....	0.355	3.550
			Mean,	3.643
0.2	0.710	0.001	0.709	3.545
0.2	0.730	0.030	0.700	3.500
0.2	0.710	....	0.710	3.550
			Mean,	3.532
0.3	1.050	0.001	1.049	3.497
0.3	1.045	0.010	1.035	3.450
0.3	1.035	....	1.035	3.450
			Mean,	3.468
0.4	1.350	0.001	1.349	3.372
0.4	1.350	0.002	1.348	3.370
0.4	1.350	0.003	1.347	3.368
			Mean,	3.370
0.5	1.670	0.001	1.669	3.338
0.5	1.675	0.001	1.674	3.348
0.5	1.675	0.001	1.674	3.348
			Mean,	3.345
1.0	3.220	....	3.220	3.220
1.0	3.200	0.003	3.197	3.197
1.0	3.200	0.001	3.199	3.199
			Mean,	3.205
1.5	4.670	0.001	4.669	3.113
1.5	4.690	....	4.690	3.127
1.5	4.650	....	4.650	3.100
			Mean,	3.113
2.0	6.150	0.004	6.146	3.073
2.0	6.150	0.002	6.148	3.076
2.0	6.110	....	6.110	3.055
			Mean,	3.068

Sodium Nitrate (Continued).

I.	II.	III.	IV.	V.
2.5	7.450	0.004	7.446	2.978
2.5	7.470	0.002	7.468	2.987
2.5	7.490	....	7.490	2.996
			Mean,	2.987
3.0	8.913	0.005	8.908	2.969
3.0	8.913	0.003	8.910	2.970
3.0	8.830	0.004	8.826	2.942
			Mean,	2.960

Potassium Nitrate.

KNO$_3$ (101.19).

I.	II.	III.	IV.	V.
0.05	0.195	0.001	0.194	3.880
0.05	0.195	....	0.195	3.900
0.05	0.195	....	0.195	3.900
			Mean,	3.893
0.1	0.360	0.001	0.359	3.590
0.1	0.365	0.002	0.363	3.630
0.1	0.370	0.004	0.366	3.660
			Mean,	3.627
0.2	0.680	0.023	0.657	3.285
0.2	0.675	0.001	0.674	3.370
0.2	0.670	0.001	0.669	3.345
			Mean,	3.333
0.3	0.985	0.002	0.983	3.277
0.3	1.010	0.038	0.972	3.240
0.3	0.985	0.001	0.984	3.280
			Mean,	3.266
0.4	1.270	....	1.270	3.175
0.4	1.290	....	1.290	3.225
0.4	1.295	0.037	1.258	3.145
			Mean,	3.182

Potassium Nitrate (Continued).

I.	II.	III.	IV.	V.
0.5	1.580	0.030	1.550	3.100
0.5	1.550	....	1.550	3.100
0.5	1.530	0.002	1.528	3.056
			Mean,	3.085
1.0	2.730	0.001	2.729	2.729
1.0	2.740	0.002	2.738	2.738
1.0	2.730	....	2.730	2.730
			Mean,	2.732

An examination of the above tables will show that a minimum exists in the molecular lowering of the freezing-point of all the acids, the base, and all the salts studied with the exception of two. In potassium nitrate and sodium nitrate the molecular lowering decreases with the concentration from the most dilute to the most concentrated solution studied, showing no trace of a minimum at any dilution. These facts will be shown more clearly when the results are plotted as curves, which will be done when the work is published in full.

Having found a minimum in the molecular lowerings of the freezing-point of water as produced by such a number of electrolytes, we determined to study the molecular conductivity of concentrated solutions of these substances, especially at those concentrations where the freezing-point minimum manifested itself.

The resistance to the passage of the current offered by such concentrated solutions is so small that a special form of cell was constructed, in which the plates were not large, and placed a considerable distance apart. This cell will be described more in detail in a later publication.

The results obtained are given in the following tables. v represents the volume of the solution; $\mu_v 0°$ the molecular conductivities of the solutions at zero degrees :

Hydrochloric Acid.

$v.$	$\mu_v 0°.$
1.000	200.32
0.667	182.35
0.500	170.19
0.400	152.38
0.333	141.87

Nitric Acid.

$v.$	$\mu_v 0°.$
1.000	194.95
0.667	184.89
0.500	169.23
0.400	155.43
0.333	140.97

Sulphuric Acid.

$v.$	$\mu_v 0°.$
1.000	253.44
0.667	221.25
0.500	199.42
0.400	178.79
0.333	155.29
0.286	135.00
0.250	118.86
0.222	100.21
0.200	86.97

Potassium Hydroxide.

$v.$	$\mu_v 0°.$
1.000	113.33
0.667	106.35
0.500	101.15
0.400	97.40

Calcium Chloride.

$v.$	$\mu_v 0°.$
1.000	71.16
0.667	62.14
0.500	53.98
0.400	44.79

Barium Chloride.

$v.$	$\mu_v 0°.$
20.000	116.05
10.000	103.79
4.000	95.94
2.000	89.24
1.333	85.27

Strontium Chloride.

$v.$	$\mu_v 0°.$
2.000	84.26
1.000	74.57
0.667	63.01
0.500	55.26

Sodium Nitrate.

$v.$	$\mu_v 0°.$
1.000	40.41
0.667	36.90
0.500	34.16
0.400	30.96

Potassium Nitrate.

$v.$	$\mu_v 0°.$
1.000	49.97
0.667	46.30

The molecular conductivities increase in every case regularly with the dilution, showing no sign of a minimum at any concentration.

We shall not discuss these results in this connection, but reserve any theoretical considerations for a later and fuller publication.

We wish to state that we are extending these investigations to a much larger number of electrolytes, and to a number of solvents, along the lines which we have been investigating in this laboratory.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIV.,
April, 1902.

ACTION OF PHOSPHORUS PENTACHLORIDE ON ANILINE.

BY J. ELLIOTT GILPIN.

In a previous paper in this JOURNAL[1] several products formed by the action of phosphorus pentachloride on aniline and its salts were described. It was shown that phosphorus pentachloride and aniline hydrochloride, when heated together, formed a compound whose composition could be represented by the formula $PCl_3(C_6H_5N)$, while the substance formed when the chloride is treated with aniline itself, at ordinary temperatures, was $PCl(C_6H_5NH)_4$. The amount of carbon in the latter compound could not be determined by the usual method, as the substance, when heated, was partly changed into a black mass which still contained carbon, but in an extremely stable form. Efforts have been made to determine the exact nature of this substance, but the results obtained lead to the conclusion that it is not a single definite substance but a mixture. When the compound

$$PCl(C_6H_5NH)_4$$
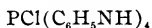
is heated it is decomposed, forming aniline and other products which escape as gases, and a black porous mass resembling coke. If this black residue is heated red hot, in a porcelain crucible, it slowly volatilizes with decomposition, but the mass shows no tendency to melt, even at that temperature, and the separate particles remain dry and retain their individual form.

[1] This JOURNAL, 19, 352.

When the crucible was heated directly in the flame of the burner so that the gases present in the flame enveloped the crucible, a flame similar to that of burning phosphorus was observed around the edge of the crucible, and a cover placed on it soon became covered on the inside with an oily liquid which soon proved to be phosphoric acid. Further experiment showed that the oxide of phosphorus, formed by the burning of the phosphorus which had been set free, combined with the water vapor in the flame to form the acid found. In order to avoid contact of the gases in the flame with the contents of the crucible, the latter was placed in a circular opening in an asbestos board which allowed the substance to be heated without being enveloped in the flame. This led to a more thorough study of the substance and its decomposition-products, in the course of which it was shown that besides phosphorus, nitrogen, hydrogen, and carbon were also present, but that specimens of the same original substance, when heated for different lengths of time, showed lack of uniformity and difference of composition.

When the substance was heated in a small porcelain tube in a stream of dry nitrogen, ammonia and a volatile substance, with an odor very similar to that of isocyanides, passed off as gases, while a very light-yellow powder, which was pure phosphorus, collected in the front end of the porcelain tube and in the condenser connected with it. Similar products were also formed when dry carbon dioxide gas was used instead of nitrogen, although apparently not so readily.

The phosphorus could be determined quantitatively by oxidation with potassium hydroxide and potassium nitrate and precipitation as ammonium magnesium phosphate, and the nitrogen by the Gunning modification of the Kjeldahl method. The percentage of nitrogen dropped from 8.87 to 8.16 and then to 7.38 per cent in successive specimens taken after heating the previous one for from fifteen to twenty minutes.

Besides the substances mentioned above, two compounds whose composition can be expressed by the formulas

$$P(NC_6H_5)_2(NHC_6H_5) \quad \text{and} \quad P_2Cl(NHC_6H_5)_7$$
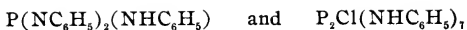
have been obtained by the action of aniline on phosphorus pentachloride under different conditions.

All efforts to replace the last chlorine atom in the pentachloride by the anilide group to form $P(NHC_6H_5)_5$ have failed. Up to the present time no conditions have been found under which all five of the chlorine atoms could be replaced by anilide residues nor could the chlorine atom in

$$PCl(NHC_6H_5)_4$$

be replaced by the aniline residue. There was no action when the $PCl(C_6H_5NH)_4$ was heated in a sealed tube with aniline alone or with aniline and some substance which would combine with the chlorine. Jackson and Mencke met with a similar difficulty in their investigation of the action of phosphorus trichloride on aniline and were also unable to replace the last chlorine atom.

The relationship to phosphorus pentachloride of the substances thus far described can be expressed by the following formulas :

$$PCl_5, \qquad PCl_3(C_6H_5N), \qquad PCl(C_6H_5NH)_4,$$
$$P(C_6H_5N)_2(C_6H_5NH), \qquad P_2Cl(C_6H_5NH)_7.$$
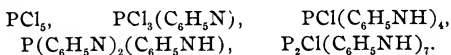
Preparation of $P(NC_6H_5)_2(NHC_6H_5)$.

About 10 grams of aniline were dissolved in 250 cc. of benzene and an equal quantity of benzene was saturated, at the ordinary temperature, with phosphorus pentachloride. Both solutions were then well cooled and were kept so while the solution of the pentachloride was slowly added to the aniline solution. After standing for some hours, the aniline hydrochloride, which had separated out, was filtered off and the product, obtained by the slow evaporation of the benzene, was washed with boiling water, in which it is entirely insoluble, to remove any soluble phosphorus compounds and most of the benzene, and then crystallized from alcohol. The substance thus obtained formed clear, well-defined crystals, which contain no water of crystallization and melt sharply at 208° to

210° (uncorr.). They belong to the orthorhombic system and show the following faces:

$$o = OP; \quad e = P; \quad m = \infty P\bar{2}; \quad b = \infty P\bar{\infty}.$$

The axial ratio is a : b : c = 0.27956 : 1 : 0.258614 and the values of the angles are as follows :

$$o \wedge e = 134° 2';$$
$$e \wedge e' = 95° 57';$$
$$e \wedge e = 158° 34';$$
$$m \wedge m = 121° 30';$$
$$m \wedge b = 119° 15';$$
$$m \wedge e = 132° 37'.$$
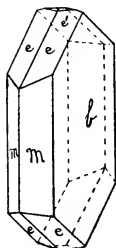
Fig. A.

This substance also crystallizes in tufts of soft, hair-like needles. The form which the crystals take is dependent upon the conditions under which the substance separates from the solution. It is, like the other substances described in these articles, quite stable and resists the action of many reagents. There is no action when it is heated with water in a sealed tube for six hours at 175° nor when heated with alcoholic potash. Aqueous potash and concentrated hydrochloric acid do not act on it, but concentrated sulphuric acid decomposes it with the formation of sulphanilic acid. Fuming nitric acid also decomposes it. An analysis of the substance gave the following results :

0.2267 gram substance gave 0.030557 gram N.

0.3469 gram substance gave 0.046082 gram N.

0.2398 gram substance gave 0.032845 gram N.
0.2537 gram substance gave 0.034127 gram N.
0.2423 gram substance gave 0.033503 gram N.
0.1647 gram substance gave 0.0588 gram $Mg_2P_2O_7$.
0.1871 gram substance gave 0.0688 gram $Mg_2P_2O_7$.
0.1642 gram substance gave 0.0575 gram $Mg_2P_2O_7$.
0.0640 gram substance gave 0.0225 gram $Mg_2P_2O_7$.

	Calculated for $P(NC_6H_5)_2(NHC_6H_5)$.	I.	II.	Found. III.	IV.	V.
N	13.77	13.47	13.28	13.69	13.41	13.82
P	10.16	....	9.92	10.27	9.78	9.82

As the same difficulty was encountered, in efforts to determine the amount of carbon and hydrogen, as in the other case mentioned above, the composition, as calculated from the results of the determination of nitrogen and phosphorus, was confirmed by determinations of the molecular weight made by the boiling-point method, using alcohol as a solvent.

Alcohol. Grams.	Substance. Grams.	Rise in boiling-point.	Molecular weight.
54.475	0.8887	0°.062	302
61.279	1.8948	0°.128	278
63.338	1.6767	0°.102	335
57.805	0.8622	0°.056	306
57.805	1.3023	0°.087	298

Mean,   303.8

Calculated for $P(NC_6H_5)_2(NHC_6H_5)$ 305

Preparation of $P_2Cl(NHC_6H_5)_7$.

By the method used for the preparation of the chlorphostetranilide ($PCl(NHC_6H_5)_4$), which consisted in adding phosphorus pentachloride to aniline at the ordinary temperature, washing the product with boiling water, and, after drying, extracting any easily soluble matter with cold alcohol, a few well-defined crystals were often obtained when the solution was allowed to evaporate slowly. These crystals had bright faces and sharp angles when first removed from the solution, but upon exposure to the air rapidly became dull, and finally crumbled to a powder. Although aniline and phosphorus

pentachloride have been brought together in various proportions and under different conditions of temperature, in order to produce this substance in quantity it has, so far, been impossible to find any conditions under which it is formed as anything more than a by-product in very small quantities.

The best yield is obtained when phosphorus pentachloride is added to boiling aniline as long as any action takes place, but even then the yield is very small, only a few crystals being formed when as much as 50 grams of aniline are used. As the formation of this substance has never been noticed when phosphorus pentachloride acts on the aniline in a cold solution, but only when the action takes place at high temperatures, it would suggest the possibility of the action being more complete if the substances could react at high temperatures. As, however, phosphorus pentachloride acts on aniline to form $PCl(NHC_6H_5)_4$ as soon as they come in contact, and further treatment with excess of either substance produces no action, the possibility of controlling the conditions so as to increase the yield of the desired product seems very slight.

After the solid, formed by the action of the phosphorus pentachloride on the boiling aniline, has cooled it is broken up and boiled with water to remove all excess of phosphorus compounds or aniline. The powdered and dry substance is then treated with a little cold alcohol which, if it is allowed to act for only a short period, dissolves out all of the easily soluble by-product, but only a small amount of the other product, which is present in very large excess.

The crystals which are formed by the slow evaporation of this solution are picked out, washed with alcohol, and dried. It is necessary to pick out each crystal and wash it with alcohol to remove the other substance, which separates out first and often sticks to the large crystals. One extraction with cold alcohol serves to remove all of the substance present in the mass. The crystals must be kept in a closed vessel over alcohol in order to preserve the luster of the faces as a few minutes' contact with the air sometimes makes them dull,

owing to the loss of the alcohol present as alcohol of crystallization. The powder obtained by driving out the alcohol melts at 192° to 194°. The substance crystallizes in the monoclinic system and exhibits a hemihedral habit. The following constants were calculated from the interfacial angles of the unit hemi-pyramids and unit prisms :

$$\beta = 87° 28'. \quad a : b : c = 1.32375 : 1 : 0.55845.$$

Planes observed :

      p   (111, —P),

      o   (11$\bar{1}$, P),

      a   (100, ∞P∞),

      b   (010, ∞P∞̀),

      m   (110, ∞P),

      x   (221, 2P) probably,

      z   (120, ∞P̀2) probably.

It exhibits a perfect cleavage parallel to the orthopinacoid ∞P∞̄ (100) and an imperfect one parallel to an orthodome, probably 2P∞̄ (201). Penetration twins were observed in a number of cases, the twinning planes being either the clinoprism ∞P̀2(120) or the orthodome 2P∞̄ (201).

The table on opposite page represents the results of a number of measurements :[1]

The following figures illustrate the different habits and twinning laws observed on the crystals :
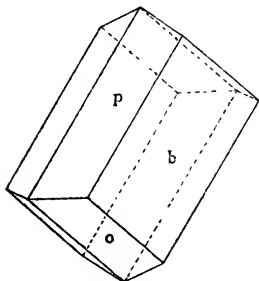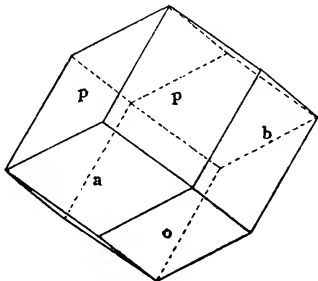
Fig. I.   Fig. II.

[1] I am indebted to Mr. A. C. Spencer for the crystallographic measurements.

Angle.	Crystal No. 1.	Crystal No. 2.	Crystal No. 3.	Crystal No. 4.	Crystal No. 5.	Crystal No. 6.	Crystal No. 7.	Crystal No. 8.	Crystal No. 9.	Crystal No. 10.	Average values.	Calculated values.	Variation.
o : p	40°31½′	40°25′	40°13′	40°13½′	40°32′	40°11½′	40°25½′	40°13′	....	....	40°20′45″	40°25′55″	+5′10″
o : o	....	....	....	....	....	54°1½′	53°33′	....	....	53°46′	53°39′30″	....	....
p : p	....	....	....	....	....	56°8′	55°20′	....	55°29′	....	55°39′00″	....	....
p : a	....	....	....	....	....	71°18′	71°47′	....	71°41′	....	71°44′00″	71°43′59″	−00′1″
p : b	....	....	....	....	....	....	61°53′	62°33′	62°17′	....	62°25′00″	62°25′00″	00
p : b	....	....	....	....	....	....	63°23½′	....	63°22′	....	63°23′00″	63°10′00″	−13′00″
o : a	67°52′	....	....	....	....	....	....	....	....	....	67°52′00″	67°50′6″	−1′54″
o : b	36°25½′	....	....	....	....	....	....	....	....	....	36°25′30″	37°5′43″	+40′13″
m : b	53°35½′	53°11′	53°25′	....	....	....	....	....	....	....	53°23′50″	52°54′17″	−29′33″
m : a	55°4′	....	....	....	....	....	....	....	....	54°30′	54°47′00″	55°31′54″	+44′54″
o : m	....	....	....	....	53°43′	....	....	....	....	53°56′	53°49′30″	54°31′38″	+42′8″
p : m	....	....	....	....	....	....	....	....	....	....			
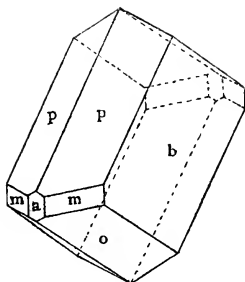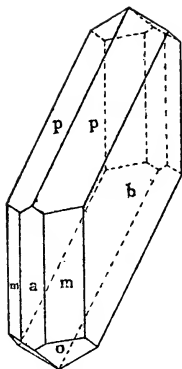
Fig. III.

Fig. IV.
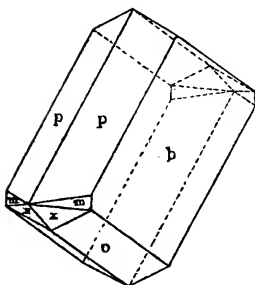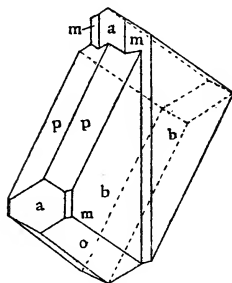
Fig. V.

Fig. VI.
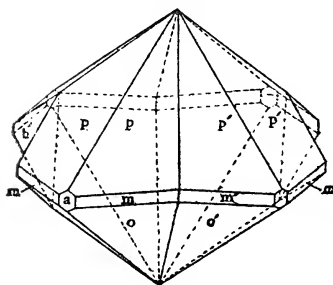
Fig. VII.
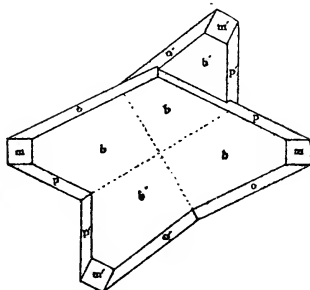
Fig. VIII.

Fig. I. shows the combination of the two hemi-pyramids with the clinopinacoid, while Fig. II. contains in addition the orthopinacoid. The equal development of the pyramids, pinacoids, and prisms gives a combination closely resembling in appearance the rhombic dodecahedron of the regular system. Figs. III. and IV. represent crystals which are alike in type but different in habit. Fig. V. represents a crystal which is tabular parallel to the clinopinacoid and in which the faces *b* and *a* are very slightly developed. In some cases, as in Fig. VI., a faulted appearance is noted and sometimes one half is smaller than the other and is placed on the face (*a*).

In Fig. VII. individuals twinned parallel to the clinoprism $\infty \overset{\backslash}{P}2(120)$ are represented, and in Fig. VIII. a projection of a twin with the orthodome $2P\overline{\infty}(201)$ as the twinning plane.

Analyses of a number of specimens of the substance gave the following results:

0.8657 gram substance lost, on heating, 0.0864 gram = 9.98 per cent.

0.3325 gram substance lost, on heating, 0.0344 gram = 10.34 per cent.

0.2026 gram substance lost, on heating, 0.0215 gram = 10.61 per cent.

0.392 gram substance lost, on heating, 0.0406 gram = 10.35 per cent.

0.4873 gram substance lost, on heating, 0.0514 gram = 10.54 per cent.

0.5121 gram substance lost, on heating, 0.0531 gram = 10.36 per cent.

0.1715 gram substance gave 19.55 cc. N at 19° and 768.9 mm. pressure.

0.335 gram substance gave 39.7 cc. N at 20°.5 and 763.2 mm. pressure.

0.1449 gram substance gave 16.9 cc. N at 11° and 763 mm. pressure.

0.1887 gram substance gave 23.3 cc. N at 19°.5 and 755 mm. pressure.

0.2878 gram substance gave 33.6 cc. N at 18°.5 and 758.6 mm. pressure.

0.1825 gram substance gave 0.0321 gram AgCl.
0.132 gram substance gave 0.0265 gram AgCl.
0.1752 gram substance gave 0.035 gram AgCl.
0.1571 gram substance gave 0.0262 gram AgCl.
0.2285 gram substance gave 0.0367 gram AgCl.
0.1406 gram substance gave 0.0423 gram $Mg_2P_2O_7$.
0.1656 gram substance gave 0.0502 gram $Mg_2P_2O_7$.
0.2733 gram substance gave 0.0822 gram $Mg_2P_2O_7$.
0.159 gram substance gave 0.048 gram $Mg_2P_2O_7$.
0.2064 gram substance gave 0.0633 gram $Mg_2P_2O_7$.
0.0882 gram substance gave 0.2186 gram CO_2.
0.113 gram substance gave 0.2788 gram CO_2.
0.1336 gram substance gave 0.3364 gram CO_2.
0.1012 gram substance gave 0.2537 gram CO_2.
0.1336 gram substance gave 0.0747 gram H_2O.
0.2506 gram substance gave 0.1275 gram H_2O.

	Calculated for $P_2Cl(NHC_6H_5)_7$.			Found.		
P	8.36	8.37	8.44	8.40	8.43	8.57
N	13.22	13.26	13.12	13.96	14.06	13.43
Cl	4.77	4.34	4.96	4.98	4.12	3.97
C	67.98	67.58	67.28	68.66	68.36	....
H	5.67	6.21	5.65	....	....	....

	Calculated for $P_2Cl(NHC_6H_5)_7 + 2C_2H_5OH$.		Found.				
C_2H_5OH	11.03	9.98	10.34	10.61	10.35	10.54	10.36

The low results obtained in the determination of the loss of alcohol of crystallization were probably due to loss while the crystals were being dried and powdered for heating, as they lose the alcohol very rapidly in contact with air. That the substance given off was alcohol was clearly shown by collecting the liquid and testing for alcohol.

While this material is easily dissolved out of the original mixture by a little cold alcohol, the powder obtained by dehydrating the crystals is only very slightly soluble in cold alcohol and, from the experiments made, appears to change to $PCl(NHC_6H_5)_4$ when boiled with alcohol so that it is impossible to purify the substance by recrystallization.

JOHNS HOPKINS UNIV.,
April, 1902.

XCV.—THE PERIODIC SYSTEM AND THE PROPERTIES OF INORGANIC COMPOUNDS.
IV.—THE SOLUBILITY OF DOUBLE SULPHATES OF THE FORMULA $M_2^I M^{II}(SO_4)_2.6H_2O$.

By James Locke.

In continuation of the plan laid out, of systematically examining, under the same conditions, the properties of analogous inorganic compounds[1] to ascertain by direct experiment what the influence of change in the atomic weights of their variable constituents may be, I wish in this paper to give the results of a study of the solubilities of the double sulphates of bivalent metals.

The series of isomorphous salts of the general formula

$$M_2^I M^{II}(SO_4)_2.6H_2O$$

is an unusually extensive one. M^I may be any alkali metal except sodium and lithium, the double sulphates of which, with bivalent metals, either contain less water of crystallization than is indicated in the above formula, or do not exist at all.[2] The place of the alkali metal may also be filled by ammonium and thallium. As representatives of M^{II} we have three members of the second family in the periodic system, magnesium, zinc, and cadmium, and also the three lightest metals in the eighth family, iron, nickel, and cobalt ; also two metals, manganese and copper, the positions of which in the system are adjacent to the above. The series thus forms an especially convenient means of studying :

1. The gradations in solubility of compounds of metals which are members of the same group in the system.

2. The relative solubility of compounds formed by elements adjacent in position to those for which such compounds conform to the degree of valence required by the system.[3]

[1] This JOURNAL, **20**, 581 ; **26**, 166, 332.

[2] It is doubtful whether any lithium salts at all can be obtained.

[3] For instance, copper, which is adjacent to zinc, the normal valence of which, according to the periodic system, is two, while that of copper is one.

3. The relative solubility of compounds of an element (Tl) the position of which is in every respect far removed from those of its analogues ; and

4. The relative behavior of the compounds of a complex radical.

A similar investigation of the alums of aluminium, vanadium, chromium, and iron, touched, so far as the trivalent metals were concerned, only the second of these points. It was found that there was no steady increase or decrease in solubility with ascending atomic weights. The order of increasing solubilities was the same for the salts of all the univalent metals, and ran :

$$Al \rightarrow Cr \rightarrow V \rightarrow Fe,$$

while that of the atomic weights is

$$Al \rightarrow V \rightarrow Cr \rightarrow Fe.$$
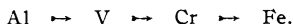
Among the alkali metals proper, the order of solubility,

$$Cs \rightarrow Rb \rightarrow K \rightarrow Na,$$

was uninfluenced by the nature of the trivalent metal, but was the reverse of that of the atomic weights. This, however, did not extend to the compounds of thallium, which in its position in the system is far removed from the alkali metals. The thallium salts all fell between those of potassium and rubidium, instead of at the end of the series. The ammonium salts, too, lay between those of rubidium and potassium, so the low molecular weight of the NH_4 radical finds no expression in the solubility of its salts. The complete order found for M^1 was

$$Cs \rightarrow Rb \rightarrow Tl \rightarrow NH_4 \rightarrow K \rightarrow Na.$$
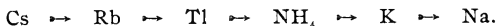
Potassium and sodium alums could be obtained only with such trivalent metals as yield the most sparingly soluble alums. The compounds Na–Fe, Na–Ga, Na–In, K–Ga, and K–In do not exist. The question arises as to whether this is due simply to the fact that such compounds would be too soluble to permit of their isolation, or to an actual difference between these metals and caesium, etc., in their power to enter into such compounds. A difference in the tendency of differ-

ent metals of a group to enter into compounds of the same general formula has not been generally recognized in the literature, and when noticed, it has usually been regarded as due simply to difference in solubility. There can be no doubt, however, but that such tendency is specific and plays a very important part in the formulas of the compounds of analogous elements. In the double sulphates with the bivalent metals, as will be seen, it can be very sharply traced.

The order of solubilities in this series stands even more in conflict with the periodic system than does that found for the alums. In answer to the above-mentioned points the data indicate that :

1. The compounds of metals in the same family of the periodic system do not follow the same or the reverse order of their atomic weights. This is true in each of the three natural groups of metals contained in the series.

2. No correlation can be found between the solubilities of the manganese and cupric salts, and the '' adjacent positions'' of these elements in the system.

3. The solubilities of the thallium salts cannot be interpreted through a consideration of that element's position, which is far removed from those of the alkali metals.

4. The influence of each alkali metal upon the solubility of its compounds is specific and retained throughout all of them. The same is true of the salts of ammonium. While conforming neither to the atomic weights of the elements nor to the molecular weights of the compounds, the solubilities stand in simple mathematical relation to one another, and that of any compound can be calculated from the constants representing the specific influence of the two metals which it contains. This being also true for the ammonium salts, it follows that in any system by which the inorganic compounds are to be exactly classified, the basis must be something which is ´as applicable to the salts of a compound radical as to an element, and which therefore cannot be the atomic weights, for these are limited to the elements alone.

In drawing this conclusion I do not wish to appear to attach too much importance to so simple a property as solubility, nor as suggesting that any system of classification be

based upon such a property alone. My results are simply an indication in a field which, except in crystallography, has been left almost untouched. The inorganic literature does not to-day contain a single instance in which complete, comparable data are at hand for all members of a series of homologous compounds, in measurement of solubility, degree of dissociation, melting-points, stability, or any other property. If we have any underlying distrust of the periodic system, it certainly does not appear to a marked extent in the literature, for except in rearrangements which leave the vital discrepancies as conspicuous as before, there has been not one attempt to correct it. To-day we know almost absolutely nothing of the gradations of properties in homologous inorganic series, except in the way of merely qualitative observations from as many different standpoints as there have been investigators of the subject. There is, then, no real possibility of extending the periodic system, or of obtaining a satisfactory new basis of classification, until quantitative data are at hand by which to judge its applicability. In the desire to ascertain how exactly gradation can be traced, I have undertaken this series of investigations, and have chosen solubility as the first property to be examined, simply because it is the most easily determined. There is probably no other one property, however, from which more information can be derived. For if a simple relation exists between the solubilities in a homologous series of hydrated double salts, then it probably follows that the same is true of the vapor-tension of their crystals, of the degree of their molecular dissociation, of the ionic dissociation of their analogous constituents, and of other properties upon which solubility presumably depends.

The methods employed for determining the solubilities was that described in my first article on the alums. The saturated solutions were evaporated to dryness at 100°, and then heated to 150° to 200° until the weight of the residual salts remained constant. This usually required about four hours. The accuracy of the method was first ascertained on a large variety of salts. In some cases the results were further confirmed by sulphuric acid determinations, or, in the case of the ammonium salts, by ignition. The ferrous salts were estima-

ted by titration with potassium permanganate. Special pre-
cautions were taken, in the case of these salts, to prevent oxi-
dation. The dried salts were introduced into the bottles, into
which a rapid current of carbon dioxide was then led, and the
salts vigorously shaken to expel all air. Without turning off
the current, the salts were then covered with water which had
been boiled a long time, and the bottles finally quickly corked.
The caesium and rubidium material used was tested from time
to time by the spectroscope.

Below I give the solubilities of all the salts of the group,
the data for which admit of comparison. The temperature
throughout was 25°, and constant within o°.1. In Table I.
the numbers express the parts by weight of the anhydrous
salts dissolved in 1 liter of water. Table II. gives the num-
ber of gram-molecules per liter, calculated from the formula

$$\frac{W}{M(a-W)},$$

in which W is the weight of the dissolved salt, a that of the
solution, and M the molecular weight of the anhydrous salt.
The atomic weights used in the calculations were: K, 39.15;
Rb, 85.4; Cs, 133; NH_4, 18; Tl, 204.1; Mg, 24.36; Mn,
55.0; Fe, 56.0; Ni, 58.7; Co, 59.0; Cu, 63.6; Zn, 65.4;
Cd, 112.0. The solubilities given represent in each case the
mean of from three to six determinations, on as many differ-
ent preparations. For the more sparingly soluble salts the
error is probably not more than 0.002 gram-molecule per
liter ; for the caesium salts it is very slightly greater.

Table I.—Parts Per Liter of Water.

	Mg.	Mn.	Fe.	Ni.	Co.	Cu.	Zn.	Cd.
Tl	...	...	...	46.1	...	81	86.0	...
Rb	202	357	242	59.8	92.8	102.8	101.0	767
K	...	...	...	68.8	128.8	116.9	131.9	...
NH_4	199	372	351	75.7	147.2	....	140.8	723
Cs	533	804	1011	255.8	418.8	460.0	386.3	1399

Table II.—Gram-Molecules Per Liter.

	Mg.	Mn.	Fe.	Ni.	Co.	Cu.	Zn.	Cd.
Tl	....	....	....	0.070	....	0.122	0.129	....
Rb	0.521	0.857	0.579	0.142	0.220	0.241	0.236	1.615
K	....	....	....	0.209	0.391	0.350	0.393	....
NH	0.791	1.321	1.044	0.264	0.513	....	0.480	2.125
Cs	1.106	1.570	1.967	0.495	0.810	0.882	0.738	2.455

Comparative researches upon this series of salts have up to the present time been confined almost entirely to the study of their crystallography. A few solubility determinations have been made upon individual compounds of the series, at different temperatures, but only one approximately thorough investigation of the subject is recorded. This was the work of Tobler,[1] who, to quote his own words, wished to ascertain "the effect caused by the substitution of an alkali sulphate for the seventh molecule of water in the vitriols, $MSO_4.7H_2O$." Needless to say, no relation between the solubilities of the simple salts and double salts could be traced. A careful examination of Tobler's work shows that his results are not very trustworthy. He finds, for instance, that the double salts containing ammonium are in every case less soluble than the corresponding potassium compounds. My own results very positively show the reverse. Our results for the ammonium salts do not differ to any great extent, and his error seems to lie more especially in those for the potassium salts. In some cases he finds the solubilities three or four times greater than my determinations indicate them to be.

	K, Ni.	K, Co.
T. Parts per liter	162	453
L. " " "	69	129

It is difficult to account for such discrepancies, even when the fact is taken into consideration that Tobler's work was done long before the newer methods for determining solubilities were known. Another instance of the unreliability of his results is seen in the fact that he obtained a very regular solubility curve for potassium ferrous sulphate, between 0° and 70°, although Küster and Thiel have since shown[2] that at about 30° there is a sharp break, representing the transition:

$$K_2Fe(SO_4)_2.6H_2O \ \rightleftarrows \ K_2Fe(SO_4)_2.4H_2O + 2H_2O.$$
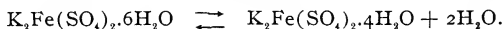
In addition to the bivalent metals mentioned above, compounds of this series are also formed by chromium[3] and vanadium,[4] but these are too unstable to permit of accurate deter-

[1] Aun. Chem. (Liebig), **95**, 193.

[2] Ztschr. anorg. Chem., **21**, 116.

[3] Péligot: Ann. chim. phys. [3], **12**, 546.

[4] Piccini: Ztschr. auorg. Chem., **19**, 204.

mination. From the remaining eight bivalent metals, forty salts are theoretically obtainable, and all but two of these, the K—Mn, and K—Cd, compounds have been described. These thirty-eight salts have all been investigated by me, although only the compounds, the solubilities of which are included in the above table, yield data that are suitable for comparison.[1] The caesium salts of all eight metals are easily obtained, although they are far more soluble than those of any other alkali metal. An indication of the much greater readiness of caesium to enter into salts of the series, as compared with potassium, for instance, is seen in the fact noted by Tutton,[2] that while several of the potassium salts are opaque, the caesium compounds of the same metals are almost invariably transparent. This is especially true of the cupric salts. Except in the case of the manganese and cadmium compounds, furthermore, no special precautions are required, with the caesium salts, to prevent the formation of salts with less water of crystallization. The salts with 6 molecules of water result within quite a wide range of temperature.

In the case of potassium, this is true only of the compounds of nickel, cobalt, copper, and zinc. The salts of the other metals form only at low temperatures, and with manganese and cadmium, where the caesium compounds are obtained with difficulty, they do not exist at all. So far as I know, this is the only instance yet noted in which the very marked tendency of caesium to enter into double salts, as compared with potassium, cannot be referred to the fact that the caesium compounds are the less soluble, and it is of particular interest for that reason. In the case of double halides a large number of caesium compounds have been prepared by Wells and others, for which no analogues of potassium can be obtained.[3] But in all such cases, I believe, the caesium salts are very difficultly soluble. The fact that the same phenomena occur when the caesium salts are the more soluble, indicates that a specific tendency for each metal must be taken into considera-

[1] The others are partially decomposed by water, with precipitation of one of their constituent salts.

[2] J. Chem. Soc. 1893, 337.

[3] As an instance may be cited the salt of quadrivalent antimony, Cs_2SbCl_6; Wells and Metzger : This JOURNAL, **26**, 268.

tion, which is not to be confused with ease of isolation, and does not invalue solubility at all. This is more or less inconsistent with the assumption by which the ionic hypothesis explains double salt formation. For, to take an instance which fully satisfies that assumption, the formation of the compound $KAg(CN)_2$ would proceed thus :

$$Ag^+ + CN^- + CN^- = Ag(CN)_2{}^-.$$
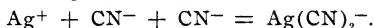
In other words, it should make no difference whether the alkali cyanide solution contains potassium ions or caesium ions, for these take no part in the reaction. Only provided the solubility products of the caesium compounds were lower than those of the potassium salts should there be any difference in the readiness with which they are obtained. We find in the double sulphates a very pronounced difference, however, although the caesium salts are in almost every instance twice as soluble, in gram-molecules, as those of potassium :

	Mg.	Mn.	Fe.	Ni.	Co.	Cu.	Zn.	Cd.
Cs	1.106	1.570	1.967	0.495	0.810	0.882	0.738	2.455
K	1.025	....	....	0.209	0.391	0.350	0.393	....

The solubility of the K,Mg salt here given does not admit of strict comparison with the others, for at 25° the salt is partially decomposed by water, separating a small proportion of its potassium sulphate. An observation to this effect had already been made by Schwarz,[1] and was confirmed by a determination of the ratio of potassium to magnesium in the residue of the saturated solution :

2.752 grams residue gave 1.2921 grams $Mg_2P_2O_7$.

Calculated, 1.0461   "   "

Ratio, K : Mg = 2 : 1.49.

No attempts were made to prepare the potassium compounds of manganese and cadmium. The fact of their non-existence seems to have been fully established by Tutton.[2] No reliable determinations, furthermore, could be made on the potassium ferrous salt. That a change of some sort takes place in this compound at 25° is indicated in the fact that after saturation is complete a fine sediment can be seen mixed with the crystals, provided the latter have not been very thor-

[1] Dingler, **198**, 159.
[2] *Loc. cit.*

oughly powdered, and this increases with the length of the digestion. I made no investigation to determine whether this is due to the separation of potassium sulphate or of the salt $K_2Fe(SO_4)_2.4H_2O$, the formation of which, according to Küster and Thiel, should take place at a very slightly higher temperature. In view of the behavior of potassium magnesium sulphate, however, it might readily be expected that the first supposition is true.

In the case of the alums, it was found that the order of solubilities of the compounds of the alkali metals proper was the reverse of that of the atomic weights of the latter. In the present series we not only find the caesium salts more soluble than those of potassium, but the rubidium salts are not intermediate between them. The solubilities of the rubidium salts

Mg.	Mn.	Fe.	Ni.	Co.	Cu.	Zn.	Cd.
0.521	0.857	0.579	0.142	0.220	0.241	0.236	1.615

are in every case well below, instead of higher than those of the corresponding potassium salts. The rubidium compounds can all be obtained within quite wide ranges of temperature, like the caesium salts, and since, in addition to this, they are much more sparingly soluble than the compounds of the other alkali metals, they are the most easily prepared and purified of all the salts examined.

The fact that for the compounds of each bivalent metal, the order in which the alkali metals fall is invariably the same,

$$Rb \rightarrowtail K \rightarrowtail Cs,$$

very clearly indicates the specific influence of the alkali metal upon the solubilities, and shows that the solubilities are not at all dependent upon the atomic weights of the alkali metals. This is further borne out by the behavior of the ammonium and thallium salts. The latter are by far the least soluble of all, although the compounds of caesium, which has the next highest atomic weight, are the most soluble.

	Mg.	Mn.	Fe.	Ni.	Co.	Cu.	Zn.	Cd.
Tl	....	....	....	0.070	....	0.122	0.129	....

As the blanks here indicate, the thallium salts could be obtained only with difficulty, in spite of their low solubility.

The salts resulted with all the bivalent metals, but those the data for which are given are the only ones on which determinations could be made. With the magnesium, manganese, iron, and cadmium compounds the separation of thallium sulphate begins as soon as water is added, and proceeds until all the sulphate of the heavy metal has passed into solution. The cobalt salt is only partially decomposed, even on prolonged digestion. In one experiment with the salt the found solubility was 0.143 gram-molecule, and the residual undissolved salt was mixed with about one-fourth its bulk of thallium sulphate.

The ammonium salts, on the other hand, stand next to caesium in their solubility, although the molecular weight of the complex (NH_4) is lower than the atomic weight of any alkali metal in the series. They are also much more readily formed than the potassium salts, although more soluble, compounds being obtainable with all the bivalent metals. The cupric salt alone is partially decomposed by water.

In view of the fact that the solubilities of the salts, even of the alkali metals proper, do not conform to the atomic weights of the latter in their order, it would obviously be idle to speculate upon the behavior of the compounds of thallium from the standpoint of that metal's position in the periodic system. Neither its position nor its atomic weight can be brought into correlation with these solubilities. The only conclusion which can be drawn without prejudice is that *the effect of each univalent metal upon the solubility of the salts is a specific one, retained throughout all its compounds in the series, and totally independent of its atomic weight.*

The same is true of the bivalent metals. In the second family, for instance, we find the order to be, not

$$Mg \rightarrowtail Zn \rightarrowtail Cd,$$
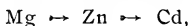
as in the atomic weights, nor the reverse, but
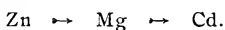
$$Zn \rightarrowtail Mg \rightarrowtail Cd.$$

	Zn.	Mg.	Cd.
Rb	0.236	0.521	1.615
NH_4	0.480	0.791	2.125
Cs	0.738	1.106	2.455

For the members of the eighth family also, the order is different from that of the atomic weights. The nickel compounds are more sparingly soluble than those of any other bivalent metal in the series, and the cobalt salts stand between these and the ferrous compounds.

	Ni.	Co.	Fe.
Rb	0.142	0.220	0.579
NH₄	0.264	0.391	1.044
Cs	0.495	0.810	1.967

Adjacent to this group is manganese on the one hand, copper on the other. The manganese salts are, in general, less
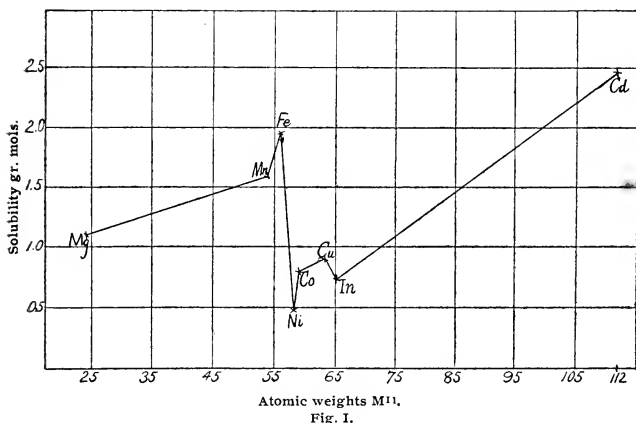
Fig. I.

soluble than those of iron, the cupric compounds more soluble than those of cobalt. For the caesium salts, for instance, we have :

	Mn.	Fe.	Co.	Cu.
Cs	1.570	1.967	0.810	0.882

Obviously, no rule can be laid down by which the solubilities can be explained by the positions of the bivalent metals. Nor can any gradation be observed according to increasing atomic weights of all the elements. The perfect independence of the solubilities from the atomic weights throughout is forcibly shown in Fig. I., where the data for the caesium salts are

plotted with the atomic weights of the bivalent metals as abscissae.

As in the case of the univalent metals, *the influence of the bivalent metal is specific, and independent of its atomic weight and of its position in the system.*

Similar conclusions had previously been reached in the case of the alums. It was there possible to calculate, indirectly, a constant which expressed this specific influence for each metal, that of one metal of the same valence being taken as the standard. Calling the difference between the solubilities of the alums of a given trivalent metal with two alkali metals, the "solubility increment" for the latter (thus, Incr. $Al_{m_2-m_1}$), it was found from the experimental data that the ratio between the corresponding increments for two trivalent metals is approximately the same, no matter which alkali metals m_2 and m_1 represent. The increment ratios,

$$\frac{\text{Incr. } V_{m_2-m_1}}{\text{Incr. } Al_{m_2-m_1}}.$$

for instance, are as follows :

Table III.

m_2.	m_1.	Ratio.
NH_4	Cs	3.18
Tl	Cs	3.39
Rb	Cs	3.41
NH_4	Rb	3.15
Tl	Rb	3.35
NH_4	Tl	3.03

The ratios between the increments for aluminium and the remaining trivalent metals are constant to about the same degree. If we adopt aluminium as a standard (the standard will below be denoted as the *initial* metal), these ratios give directly the effect produced by the substitution of the other trivalent metals for aluminium in the salts of the latter. Assuming that the variations in the ratios are due to experimental error, it follows that as soon as the solubilities of two corresponding salts of each trivalent metal are known the others can be calculated. I thought it probable that the same would be true of the salts of the bivalent metals, but found

that in this case there can be no thought of a constant increment ratio. For the series cobalt-nickel (nickel being taken as the initial metal) the following increment ratios were obtained :

Table IV.

m_2.	m_1.	Ratios.
Cs	Rb	1.67
Cs	K	1.46
Cs	NH$_4$	1.26
NH$_4$	Rb	2.40
NH$_4$	K	2.21
K	Rb	2.55

These variations in the increment-ratios are satisfactorily explained, however, if we assume that three solubilities for each bivalent metal must be known, instead of two. It has been found that the relation between the solubilities of corresponding salts of any two bivalent metals is very exactly expressed by the quadratic equation,

$$(1) \quad y^1 = ay^2 + 2by + c,$$

in which y and y' are the salts of two bivalent metals with the same univalent metal.

The constants a, b, and c readily admit of chemical interpretation. If y'_1, y_1, y'_2, y_2, and y'_3, y_3 are three solutions of this equation, then,

$$y'_1 = ay_1^2 + 2by_1 + c,$$
$$y'_2 = ay_2^2 + 2by_2 + c,$$
$$y'_3 = ay_3^2 + 2by_3 + c,$$

from which, after subtraction, we obtain,

$$(2) \quad \begin{cases} \dfrac{y'_1 - y'_2}{y_1 - y_2} = a(y_1 + y_2) + 2b \\[2mm] \dfrac{y'_2 - y'_3}{y_2 - y_3} = a(y_2 + y_3) + 2b \end{cases}.$$

Eliminating b, the expression for a becomes,

$$a = \dfrac{\dfrac{y'_1 - y'_2}{y_1 - y_2} - \dfrac{y'_2 - y'_3}{y_2 - y_3}}{y_1 - y_3}.$$

That is, a is the average rate of change of the increment ratios.

The constant $2b$ is the limit to which the increment ratios approach. In the equation (2) it is given as the increment ratio minus the product of a into the sum of the solubilities of the two salts of the initial bivalent metal. If a is zero, then the increment ratio becomes $2b$, and is, therefore, constant. This was the assumption tacitly made in the mathematical treatment of the solubilities of the alums. The increment ratio approaches more closely to $2b$, furthermore, the less the solubilities of the two salts of the initial element $(y_1 + y_2)$ are, the correction in that case being very small. It is probable, therefore, that in salt series of which the members are very sparingly soluble, the general relation would hold approximately true:

$$\frac{y'_1 - y'_2}{y_1 - y_2} = 2b.$$

If in the equation

$$y' = ay^2 + 2by + c,$$

we set $y = 0$, then $y' = c$, whence it follows that c would be the solubility of a salt of the second bivalent metal when that of the corresponding compound of the initial metal is zero. In the tables given below, the values for c were calculated from the equation

$$c = y'_1 - y_1 \frac{y'_1 - y'_2}{y_1 - y_2} + ay_1y_2.$$

For the derivation of the values of these constants three solubilities must, of course, be known for each bivalent metal, and a fourth is necessary to test their validity. Unfortunately, data can be obtained for four or more salts only in the case of nickel, cobalt, copper, and zinc. With these salts the agreement between the values of each constant, when derived from different solubilities, is remarkable. In the following tables nickel has been retained as the initial bivalent metal throughout, not only because the solubilities of its salts with all the univalent metals could be measured, but because, being the least soluble of all, their determination was the least

subject to experimental error. Under y_1, y_2, y_3, are given the various combinations of salts by which the constants are derived. The values for c are expressed in thousandths of gram-molecules per liter. The columns i give the increment ratios as observed, and as calculated from the equations (2), using for a and b the values marked by asterisks. The observed increment ratios are uncertain by one or two units in the second decimal, and the difference between the observed and calculated values for them are therefore well within the limit of error.

Table V.—Nickel-Cobalt.

y_1.	y_2.	y_3.	a.	2b.	c.	i.	i. Observed.
Cs	NH$_4$	Rb	—0.00320*	3.70	—243	1.27	1.26
Cs	NH$_4$	K	—0.00325	....	....	....	....
Cs	K	Rb	—0.00313	3.70	—244	1.45	1.46
NH$_4$	K	Rb	—0.00300	3.72	—247	2.19	2.21
Cs	Rb	..	....	3.70*	—239*	1.66	1.67
NH$_4$	Rb	..	....	3.70	—240	2.40	2.40
K	Rb	..	....	3.80	—237	2.58	2.55

Table VI.—Nickel-Copper.

y_1.	y_2.	y_3.	a.	2b.	c.	i.	i. Observed.
Cs	K	Tl	+0.0005*	1.52	+12	1.87	1.86
Cs	K	Rb	+0.0005	....	....	....	....
K	Rb	Tl	+0.0002	1.51	+14	1.69	1.68
Cs	Rb	Tl	+0.0005	1.51	+16	1.83	1.82
Cs	Tl	..	....	1.52*	+13*	1.80	1.79
K	Tl	..	....	1.50	+15	1.65	1.64
Rb	Tl	..	....	1.54	+13	1.63	1.65

Table VII.—Nickel-Zinc.

y_1.	y_2.	y_3.	a.	2b.	c.	i.	i. Observed.
Cs	NH$_4$	K	—0.0016	2.33	—26	1.12	1.12
Cs	NH$_4$	Tl	—0.0016*	....	....	....	....
Cs	K	Tl	—0.0016	2.33	—26	1.20	1.20
NH$_4$	K	Tl	—0.0015	2.34	—25	1.57	1.58
Cs	Tl	..	....	2.33*	—26*	1.43	1.43
NH$_4$	Tl	..	....	2.33	—26	1.81	1.80
K	Tl	..	....	2.34	—27	1.89	1.90

The most reliable values for the three constants are those marked by asterisks, the increments $y_1 - y_2$ and $y_2 - y_3$ being

there the largest, and consequently the least influenced by experimental error. Adopting these values, we have, as the expression of the relation which the solubilities of the salts of cobalt, copper, and zinc bear to those of nickel, the equations :

$$y_{Co} = 3.70 \ y - 0.0032 \ y^2 - 0.239 ;$$
$$y_{Cu} = 1.52 \ y + 0.0005 \ y^2 + 0.013 ;$$
$$y_{Zn} = 2.33 \ y - 0.0016 \ y^2 - 0.026.$$

The value for a, it will be seen, is in each case very small, and in the nickel-copper series, where it is only $+0.0005$, the increment ratios approach very closely to the value of $2b$ itself.

Since these equations are satisfied by the solubilities of the salts of any alkali metal, all that is necessary to obtain a measure for the influence of any alkali metal upon its compounds is to adopt the nickel salt of one of these as a standard, and substitute for this value of y the product my, where m is the ratio between the solubilities of the standard salt and second salt of nickel. In the form

$$y_{M^{II}} = am^2 y^2 + 2bmy + c,$$

then, the general formula would give, by the substitution of corresponding values for the univalent and bivalent metals, respectively, the solubility of any salt in the series. Adopting caesium nickel sulphate as a standard, the values for m are :

	Cs.	NH₄.	K.	Rb.	Tl.
m	1.00	0.533	0.422	0.287	0.141

These constants give the following solubilities in the cobalt, copper, and zinc series. Under D is given the difference from the observed solubilities :

Table VIII.

	Co.	D.	Cu.	D.	Zn.	D.
Tl	....	....	0.122	0.000	0.130	+0.001
Rb	0.222	+0.002	0.239	—0.002	0.270	+0.034
K	0.394	+0.003	0.352	+0.002	0.392	—0.001
NH₄	0.515	+0.002	....	....	0.478	—0.002
Cs	0.808	—0.002	0.887	+0.005	0.738	0.000

There is but one instance, that of the zinc-rubidium salt, in

which the error exceeds that of experimental error. In the other cases of abnormal solubility noted in the course of the work, it has been possible to trace the difference to more or less complete decomposition by water, with separation of one of the constituent salts; but for the error in this case I am unable to account. Its magnitude is not very great, however, and in view of the remarkable coincidence between calculated and observed results throughout the rest of the table, may, for the time being, be disregarded. I hope later to make a special examination of the various zinc salts, with the object of ascertaining its cause. The validity of the relation between the solubility of the salts in general is emphatically shown by the fact that I was able to prophesy the solubilities of some of the compounds in the series within the limit of error, before they had been made at all.

Of course, the above general equation would give the solubility of a salt of zinc, etc., for any value of y whatsoever, without regard to whether the corresponding nickel compound actually exists or not. The possible values for y, however, are limited by a strange rule, which must, for the time being, be regarded as purely empirical, as it does not hold in the case of the alums. The solubilities of the salts of any given bivalent metal satisfy the equation

$$M_{11} \frac{Cs - m_1^i}{Cs - m_2^i} = n^e,$$

where n is a constant, and the exponent e is 1, 2, or 3, according to how far removed from one another the salts of the metals M_1^i and M_2^i are in the order of solubilities

$$Cs \ \rightarrowtail \ NH_4 \ \rightarrowtail \ K \ \rightarrowtail \ Rb \ \rightarrowtail \ Tl.$$
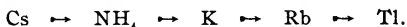
The accuracy of the rule is shown by the ratios given in

Table IX.

	e.	Ni.	Co.	Cu.	Zn.
$\dfrac{Cs-NH_4}{CS-K}$	1	0.81	0.71	....	0.75
$\dfrac{Cs-K}{Cs-Rb}$	1	0.81	0.70	0.83	0.70

	$e.$	Ni.	Co.	Cu.	Zn.
$\dfrac{Cs-Rb}{Cs-Tl}$	1	0.83	....	0.84	0.82[1]
$\dfrac{Cs-NH_4}{Cs-Rb}$	2	0.81	0.71	....	0.72
$\dfrac{Cs-NH_4}{Cs-Tl}$	3	0.81	....	....	0.75
$\dfrac{Cs-K}{Cs-Tl}$	2	0.82	....	0.84	0.75

The agreement between the calculated and observed incre-
ment ratios for the different bivalent metals, as given in Tables
V. to VII., is very much more exact than that found in the
case of the alums, Table IV., when the ratio was assumed to
be constant. This led me to test the solubilities of the alums
by the above quadratic equation. In my previous article, as
has been stated, the tacit assumption had been made that a
here equals zero, in which case the increment ratio is con-
stant, and equals $2b$. It was found that a somewhat more ex-
act expression for the solubilities in this series as well, was
obtained by the new formula, although a is in fact much
smaller in each case than for the double sulphates of any
of the bivalent metals except copper. It will suffice here
to give the values for a, b, and c for a single one of the alum
series. In that of aluminium-vanadium, aluminium being
taken as the initial trivalent metal, these values are as fol-
lows :

Table X.—Aluminium-Vanadium.

y_1.	y_2.	y_3.	$a.$	$2b.$	$c.$	$i.$	i Observed.
NH_4	Tl	Rb	—0.0009	3.54	—26	3.03	3.03
NH_4	Tl	Cs	—0.0009*	....	....	....	....
NH_4	Rb	Cs	—0.0008	3.55	—29	3.14	3.15
Tl	Rb	Cs	—0.0007	3.56	—29	3.33	3.35
NH_4	Cs	..	....	3.54*	—25*	3.18	3.18
Tl	Cs	..	....	3.52	—29	3.37	3.39
Rb	Cs	..	....	3.47	—25	3.47	3.41

[1] The variations here are due to the slightly abnormal solubility of the zinc-
rubidium salt. Using for the latter the calculated solubility (Table VIII.) the ratios
into which this salt enters are

$$\frac{Cs-K}{Cs-Rb} = 0.74, \qquad \frac{Cs-Rb}{Cs-Tl} = 0.75, \qquad \frac{Cs-NH_4}{Cs-Rb} = (0.74)^2,$$

in close agreement with the ratios for the other salts.

Using the equation

$$y_v = 3.54\ y - 0.0009\ y^2 - 0.025,$$

the calculated solubilities for the vanadium alums are as follows :

Cs.	Rb.	Tl.	NH₄.
0.020	0.180	0.573	1.211
D = 0.000	+0.003	0.000	+0.001

For the aluminium-chromium and aluminium-ferric series, similarly, the equations

$$y_{Cr} = 1.37\ y - 0.0008\ y^2 - 0.002$$
$$y_{Fe} = 4.84\ y - 0.0013\ y^2 - 0.019$$

form a much more exact expression for the solubilities of the chromium and ferric alums than did that previously derived.

The relations discussed above indicate very conclusively that *in a group of isomorphous compounds the effect of a given element upon the solubility of its compounds in the series is constant throughout all these compounds.* The general formula for its calculation is the same for the salts of both bivalent and trivalent metals, and in all probability, therefore, we have before us the working, in two instances, of a general law, which, after development in other series, may be of very great importance in the systematization of inorganic compounds.

The general applicability of an equation of the form

$$y' = ay^2 + 2by + c$$

shows that if the solubilities be plotted with the salts of the initial element as ordinates, and those of the second metal as abscissae, a parabola always results. Fig. II. gives its form for the aluminium-vanadium series among the alums, and for the nickel-cobalt, nickel-copper, and nickel-zinc series in the other group. It will be seen that in the aluminium-vanadium and nickel-copper series, where the values of *a* are extremely small (—0.0009 and +0.0005, respectively), the parabolas very nearly approach to being straight lines.

This method of presentation is of peculiar interest, because in it no account whatsoever is taken of the atomic weights. The latter do not even enter into the values of *a* and *b*, which

Fig. II.
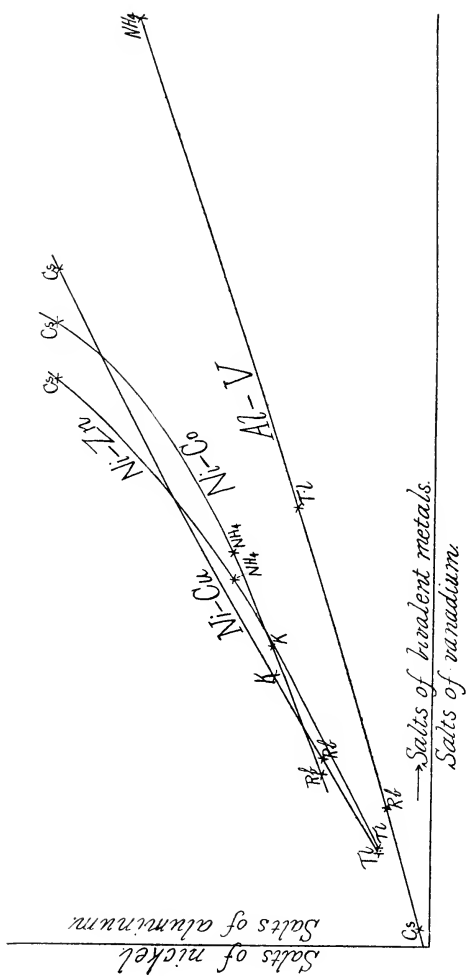
determine the form of the parabolas, and are calculated merely from the increment ratios. The repeated crossings of the curves for the different bivalent metals, furthermore, show that there is no correlation between solubilities and atomic weights, except in the fact that the former are expressed in gram-molecules. For certain reasons which will appear later, however, it is better to adhere to the more conventional means of presentation, using the solubilities as ordinates and atomic weights as abscissae.

This was the method employed in my articles on the alums, in which, for abscissae, the atomic weights of the trivalent metals were chosen. If a were zero, the lines connecting the solubility-points of the alums of two trivalent metals with the same univalent metal, as in Fig. I., would then have a common point of intersection. This assumption was made the basis of my calculations in that paper. When a is too large to be neglected, however, these lines, as will be shown, instead of meeting in a point, are tangential to a hyperbola, one of the asymptotes of which is the perpendicular erected at the x-value for the initial element.

If the atomic weight of nickel be represented by σ, and that of a second bivalent metal by $\sigma + h$, and the solubilities of the salts of the two with a given univalent metal be y and y', respectively, then the equation of the line joining y and y' will be :

$$(3) \quad \frac{Y-y}{X-\sigma} = \frac{y'-y}{h}.$$

Taking two new corresponding solubilities, $y + \Delta y$, and $y' + \Delta y'$, we find for the point of intersection of the line (3) with that joining the new points,

$$(4) \quad \begin{aligned} X &= \sigma + \frac{h}{1 - \dfrac{\Delta y'}{\Delta y}} \\[2em] Y &= \frac{y' - y\dfrac{\Delta y'}{\Delta y}}{1 - \dfrac{\Delta y'}{\Delta y}} \end{aligned}$$

Since the equation

$$(5) \quad y' = ay^2 + 2by + c$$

is also satisfied by $y + \Delta y$, $y' + \Delta y'$,

$$(6) \quad y' + \Delta y' = a(y + \Delta y)^2 + 2b(y + \Delta y) + c.$$

After subtracting (5), therefore,

$$(7) \quad \frac{\Delta y'}{\Delta y} = 2ay + 2b + a\Delta y.$$

Now let the two lines in question approach coincidence. As Δy approaches zero, from (7), $\frac{\Delta y'}{\Delta y}$ becomes $2ay + 2b$. Substituting this value in (4), the point (X, Y),

$$
(8) \quad
\begin{aligned}
X &= \sigma + \frac{h}{1 - 2(ay + b)} \\
Y &= -\frac{ay^2 - c}{1 - 2(ay + b)}
\end{aligned}
,
$$

becomes the point of contact of the line joining (σ, y), $(\sigma + h, y')$ with the curve touched by *all* lines joining corresponding values of y and y', or corresponding solubility-points. The equation of this curve, which is an hyperbola, may be found by eliminating y in (8). This gives

$$(9) \quad K^2(x - \sigma)^2 + 4ah(X - \sigma)Y - 2h(1 - 2b)(X - \sigma) + h^2 = 0,$$

where

$$K^2 = (1 - 2b)^2 - 4ac.$$

The center is the point $\left(\sigma, \frac{1 - 2b}{4a}\right)$ and the asymptotes are :

$$x = \sigma, \quad K^2(x - \sigma) + 4ahY - 2h(1 - 2b) = 0.$$

The tangents parallel to the x-axis touch at the points :

$$\left(\sigma \mp \frac{h}{k}, \quad \frac{1 - 2b}{2a} \pm \frac{K}{2a}\right),$$

and from these data the curve may be located, and by (8), as many points located thereon as we wish.

In the cases before us, the hyperbolas are all very thin. A peculiar fact, in the series nickel-cobalt and nickel-zinc, is

that the lines connecting the caesium salts are tangential to one branch of the curve, those for the remaining salts to the other. In both these series the upper branch lies to the right of the nickel perpendicular. In the nickel-copper series, on the other hand, the upper branch lies to the left, and all the lines are tangential to this. This case is represented in Fig. III.
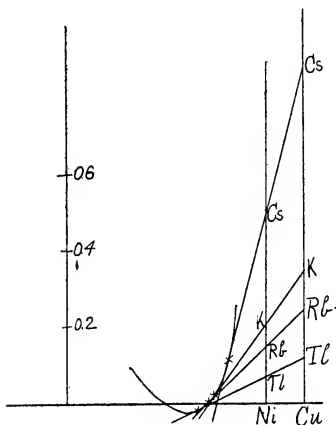
Fig. III.

A consideration of this figure brings out one very important point, not shown by the first and simpler method of plotting, and for the purpose of illustrating which, therefore, this method has been retained. In the nickel-copper series all the lines are tangent to the curve at points lying on the same side of that at which it is touched by the horizontal tangent, and the curve lies outside the two perpendiculars. All these lines are, therefore, inclined upward, and the solubility of each cupric salt, accordingly, is greater than that of the corresponding nickel compound. This, however, is by no means necessarily the case. If the hyperbola, or that part of it included between the points of tangency, lay between the two perpendiculars, then (Fig. IV.) if the successive solubilities of the salts of the initial element ran A ↦ B ↦ C, those of the second

would lie in the order $C_1 \rightarrowtail B_1 \rightarrowtail A_1$. The order of solubility would be reversed throughout. The most soluble compounds
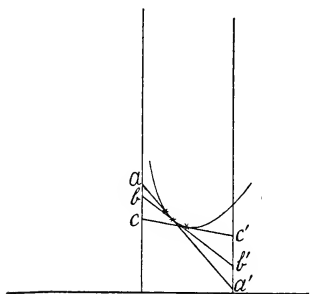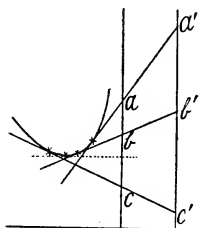
Fig. IV.   Fig. V.

for the initial element would be the least soluble for the second. This is the most complicated case, and has not yet, with certainty, been observed.

With the hyperbola lying outside the perpendiculars, secondly, let us assume its position to be such that the y-value of the horizontal tangent is intermediate between the extremes of solubility for the compounds of the initial element. *Then (Fig. V.), for all points lying below the horizontal the solubilities for the second element will be less than for the first, and for those above it they will be greater.* In the figure we have $A < A_1$, $B < B_1$, but $C > C_1$. Two instances are shown by the compounds of the bivalent metals in which this interesting relation occurs : in both, the extreme solubilities for the initial element are in the one case less, in the other case greater, than those for the second. In the zinc-copper series we find :

$$Zn\text{–}Tl \quad 0.129 \quad > \quad Cu\text{–}Tl \quad 0.122 ;$$
$$Zn\text{–}Cs \quad 0.738 \quad < \quad Cu\text{–}Cs \quad 0.882.$$

In the zinc-cobalt series :

$$Zn\text{–}Rb \quad 0.236 \quad > \quad Co\text{–}Rb \quad 0.220 ;$$
$$Zn\text{–}Cs \quad 0.738 \quad < \quad Co\text{–}Cs \quad 0.810.$$

Examined alone, these figures apparently stand at utter variance to one another, and seem to forbid all possibility of our

ever measuring the influence of an element upon its compounds in properties which are not strictly additive. It is probably due largely to such apparent contradictions, of which the literature is full, that so little work has been done toward the exact systematization of inorganic chemistry. But these solubilities represent merely certain points in a general scheme. Taken alone, no theoretical importance can be attached to them as a measure of the influence of zinc or cobalt upon their compounds, for to judge by the caesium salts would be to disregard the opposite relation of the rubidium compounds. As soon as more solubility-points for the two bivalent metals have been determined, however, these inconsistent data are explained, and we obtain from the solubility increments an equation which gives the solubilities not only of the caesium and rubidium salts, but of all.

The lack of any relation between the solubilities and the positions of the elements in the periodic system, or their atomic weights, renders the behavior of the ammonium salts important, for if atomic weight is not the determining cause of the varying solubilities, then there is no need of distinguishing the compounds of a complex radical from those of elements pure and simple, in any reactions which do not involve the decomposition of the radical itself. The ammonium salts follow exactly the same law as do the salts of the alkali metals, and in any exact and complete system of classification, therefore, they are as much entitled to a place as the metallic salts. The correct basis for classification, then, cannot be the atomic weights, for ammonium has no atomic weight. The periodic system ignores all resemblance between ammonium compounds and those of the alkali metals. For the purpose of rough, temporary classification this is all very well. It is sufficient to regard the ammonium salts as ''imitating'' the metals. But if we wish to make our system a guide toward ascertaining what the actual determining cause of the properties of inorganic compounds is, we must seek one which will include complex radicals, and which, incidentally, will differentiate between the compounds of an element in different degrees of oxidation.

Such a system is to-day impossible, for we know with ex-

actitude almost nothing concerning gradation in the properties of inorganic compounds. But if the influence of an element upon its compounds of a series is constant throughout, as from the above work appears to be the case in the matter of solubility, then the thought of an exact system is not very visionary. To attain it, however, analogous compounds must be given consistent comparative study, and quantitative data be obtained concerning them. In each series of compounds studied, furthermore, it is of prime importance to include as many representatives of the variable elements or groups as possible. The relative solubilities of the thallium and caesium double sulphates of zinc and copper, and of the rubidium and caesium salts of zinc and cobalt, show that no definite information can be gained of the influence of an element upon its compounds until at least three salts of each metal have been examined. A fourth or a fifth must be examined to prove the validity of the deductions drawn on the basis of the data thus obtained. To-day, so far as I can ascertain, there is not a single instance in the inorganic literature, where a property like solubility has been accurately determined for the fourth salt in such a series. There are almost no cases, where comparable and reliable data for three are at hand. The most essential features of the periodic system have hardly ever been tested by quantitative measurements.

The conclusions drawn in this paper regarding the independence of the solubilities from the atomic weights is open to criticism upon one point, which arises in this connection. To ascertain the influence of a given bivalent metal upon the double sulphate, we must know the solubility of at least three salts of both this and the initial metal. But the data thus derived are in a measure comparable with those which would be obtained from a consideration of the salts with a single alkali metal, for in the SO_4^{--} group we are adhering to one representative of another variable constituent. It is barely possible that after a similar examination of the corresponding selenates, a combination of the constants obtained in the two series, which would thus give the influence of the metal upon any of its compounds in the series $M_2^I M^{II} (RO_4)_2 . 6H_2O$, would bring the metals into the order of their atomic weights.

Unfortunately, except in the one compound,

$$(NH_4)_2Mg(CrO_4)_2.6H_2O,[1]$$
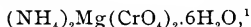
R is represented only by sulphur and selenium, and for accurate comparison three substituent elements are necessary. Two much more suitable series for the investigation of this point would be the salts of the general formulas $M_2^IM^{IV}X_6$ and $M^{II}M^{IV}X_6.6H_2O$, in which all three symbols have several representatives. The second formula should theoretically be conformed to by 192 different salts. These two series I should like to reserve to myself for future study.

My thanks are due to Professor Percy F. Smith, of the Sheffield Scientific School, for many suggestions embodied in the mathematical part of the above work.

NEW HAVEN, April 2, 1902.

THE INACTIVITY OF LIPASE TOWARDS THE SALTS OF CERTAIN ACID ETHERS CONSIDERED IN THE LIGHT OF THE THEORY OF ELECTROLYTIC DISSOCIATION.

BY J. H. KASTLE.

While studying the kinetics of lipolytic hydrolysis, a subject that has been under investigation in this laboratory now for some time, it was thought desirable to try the effect of varying amounts of water on the hydrolysis of ethereal salts by lipase. In order to accomplish this satisfactorily it was found necessary to employ a very soluble ethereal salt and one which the ferment could readily hydrolyze. On account of the solubility of certain salts of some of the acid ethers it seemed probable that these substances might be employed to advantage in the investigation of this particular phase of the problem. Such a substance is sodium ethyl succinate. The fact that diethyl succinate is readily hydrolyzed by lipase furnished an additional reason for using sodium ethyl succinate in the preliminary experiments. While this salt was never obtained in as satisfactory a condition of purity as could be desired, it was observed that lipase could not effect its

[1] Grailich, A. W., **27**, 175. The potassium compound crystallizes with $2H_2O$.

hydrolysis. This seemed the more remarkable in view of the ease with which the diethyl succinate is hydrolyzed by the lipolytic ferment.

In view of this somewhat remarkable and interesting result it seemed advisable to test the conduct of lipase towards the salts of other acid ethers, and also, by way of comparison, its action on the corresponding neutral ethers.[1] Up to the present the action of the ferment on the mono- and diethyl ethers of eight dibasic acids has been studied. The following results were obtained:

Fumarates.—Diethyl fumarate is very readily hydrolyzed by lipase. This has been demonstrated by numerous experiments. On sodium ethyl fumarate, on the other hand, lipase is without action in twenty-four hours, at 40° C.

Oxalates.—Diethyl oxalate is so easily hydrolyzed, even by pure water, that it was found difficult to determine whether lipase accelerated the hydrolysis. By working at 0° C., however, it was observed that the active ferment accelerates the hydrolysis.

On potassium ethyl oxalate lipase has no action, or, if any, it retards the hydrolysis. Tubes containing small amounts of this salt and strong unfiltered hepatic extracts, and the boiled controls showed no difference in acidity in twenty-four hours at 40° C. On the other hand, with clear, weaker solutions of hepatic lipase and this salt, the boiled controls showed a slight acidity after twenty-four hours at 40° C., whereas the tubes containing the active ferment remained neutral.

Phthalates.—Diethyl phthalate is slowly hydrolyzed by lipase. This has been proved in numerous experiments. On the other hand, it is not acted on by pure water at ordinary temperatures or at 40° C. in twenty-four hours.

[1] In testing the conduct of lipase towards the various ethers employed in this investigation the following mode of procedure was generally adopted. Tubes were prepared containing 5 cc. of the active and boiled enzyme. To these litmus was added, together with small amounts of the ether to be tested and a small quantity of toluene as antiseptic. The tubes were then kept at the proper temperature, for the desired interval, any hydrolysis being indicated by the change in color of the litmus. The activity of all lipase extracts and solutions employed in the investigation was repeatedly determined by means of ethyl butyrate during the progress of the work. The solutions and extracts employed were found to hydrolyze 0.0058 to 0.0290 gram of ethyl butyrate in fifteen minutes at 40° C., when 5 cc. of the solution or extract were allowed to act on 0.2300 gram of the ethereal salt.

Barium ethyl phthalate is not hydrolyzed by lipase at ordinary temperature or at 40° C. in twenty-four hours. That such is the case has been demonstrated both with clear and unfiltered extracts of the ferment acting under a variety of conditions. Similar results have been obtained with potassium ethyl phthalate.

p-Nitrosulphobenzoates.—Like most, if not all, of the sulphonic ethers, diethyl *p*-nitrosulphobenzoate is slowly hydrolyzed by pure water. Apparently, lipase does not accelerate the hydrolysis of this ether. In fact, it has been found that clear, dilute solutions of lipase seem rather to retard the hydrolysis than otherwise. On the other hand, with more active unfiltered pancreatic and hepatic extracts the diethyl ether showed no hydrolysis in twenty-four hours at 38° C.

It has also been shown that neither the barium *p*-nitrosulphobenzoate nor the potassium salt were hydrolyzed by any of the lipase extracts in twenty-four hours at 38° C.

p-Sulphobenzoates.—The monoethyl ether of *p*-sulphobenzoic acid was prepared by passing hydrochloric acid gas into a solution of the acid in absolute alcohol. The excess of alcohol, together with the hydrochloric acid, was evaporated off on the water-bath, the residual syrup diluted with a considerable quantity of water, and neutralized with barium carbonate. The excess of barium carbonate was then filtered off and the filtrate evaporated to crystallization. Barium ethyl *p*-sulphobenzoate was thus obtained in the form of beautiful, thin, white plates. On analysis the salt gave numbers agreeing with the theory for

$$p\text{-}\left(C_6H_4\underset{SO_2O}{\overset{COOC_2H_5}{\diagdown}}\right)_2Ba + 1\tfrac{1}{2}H_2O.$$
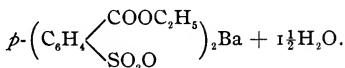
This salt was found to be unacted on by lipase.

The conduct of diethyl *p*-sulphobenzoate has not been determined.

Sulphates.—During the last two years a great many attempts have been made in this laboratory to effect the hydrolysis of barium and potassium ethyl sulphate by means of lipase. All these have resulted in failure. The ferment has

always been found to be inactive towards these salts. The conduct of the ferment towards diethyl sulphate has not been tested.

From these observations one might get the impression that possibly the salts of these various acid ethers are toxic to lipase and that they thereby prevented its action. That such, however, is not the case has been proved by adding small amounts of ethyl butyrate to the contents of the tubes before the conclusion of the tests. In every instance the tubes containing the active ferment showed a marked hydrolysis in a few minutes after the addition of the butyrate, whereas the control experiments gave no evidence of any hydrolysis. In this way it was shown that even after remaining in contact with the salts of these acid ethers for twenty-four hours, or even longer, the ferment was capable of hydrolyzing ethyl butyrate.[1]

This would seem to indicate that the failure on the part of the lipolytic ferment to hydrolyze the salts of acid ethers cannot be ascribed to the toxicity of these substances, but must be due to some other cause. Apparently, the explanation of the difference in the conduct of lipase towards the neutral and acid ethers is to be looked for not in any specific effect which either of these substances may exert toward the ferment, but rather in some fundamental chemical difference in the nature of the two classes of ethereal salts. In this peculiar conduct on the part of lipase we are reminded, at least to some extent, of the remarkable behavior of glucose and emulsine towards α- and β-methyl glucoside. In order to account for the remarkable difference in the conduct of the two ferments to these compounds it has been found necessary to refer it to a corresponding difference in the stereo-configuration of the two glucosides; so in the same way it would seem logical to assume that the difference observed in the conduct of lipase towards neutral ethers and the salts of acid ethers is due in all

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[1] It is not intended to convey by this that the salts of the acid ethers are altogether non-toxic to lipase. Like all salts, even including such substances as sodium and potassium chlorides, they have been observed to be somewhat toxic in their effect upon the ferment; but in no case has there been an entire loss of lipolytic activity on the part of any solution of lipase employed in these experiments, as the result of the poisonous action of the substance being tested.

probability to some inherent chemical difference in the nature of these two classes of compounds.

In the light of our present conceptions the most characteristic difference between the diethyl ether of a dibasic acid and a metallic salt of the monoethyl ether of the same acid, so far as their chemical conduct is concerned, is that in aqueous solution the latter is ionized whereas the former is not. This difference is quite as fundamental as a structural one. Might it not account, therefore, for the difference in their conduct towards lipase ?

In view of this it became a matter of interest to test the conduct of lipase towards certain derivatives of the monoethyl ethers that are chemically indifferent. Accordingly, ethyl oxamate and ethyl *p*-sulphaminebenzoate were prepared and their conduct towards lipase tested in the usual manner. Both of them were found to be hydrolyzable by the action of the ferment. Briefly, then, the facts as they are known to us at present are these :

First, lipase has been found to hydrolyze a large number of neutral ethers. Among those whose conduct towards the ferment has been tested in this laboratory may be mentioned the following : Ethyl formate, ethyl acetate, ethyl butyrate, ethyl propionate, ethyl isobutyrate, ethyl benzoate, methyl butyrate, amyl acetate, amyl butyrate, diethyl succinate, diethyl oxalate, diethyl fumarate, diethyl tartrate, diethyl phthalate, etc.

Secondly, lipase has been found to be inactive towards the salts of acid ethers, the following having been tested with the ferment : Sodium ethyl succinate, potassium ethyl oxalate, barium ethyl sulphate, potassium ethyl sulphate, barium ethyl phthalate, potassium ethyl phthalate, barium ethyl *p*-sulphobenzoate, sodium ethyl fumarate, barium ethyl *p*-nitrosulphobenzoate, potassium ethyl *p*-nitrosulphobenzoate. Not one of these compounds was hydrolyzed by the ferment.

Thirdly, lipase has been found capable of hydrolyzing chemically indifferent derivatives of certain of the monoethyl ethers, such as ethyl oxamate and ethyl *p*-sulphaminebenzoate.

In the light of these results one is naturally led to connect the inactivity on the part of lipase towards the salts of acid ethers with the electrolytic dissociation of these substances in aqueous solution ; and upon the assumption that the hydrolysis of a substance by means of a ferment is always preceded by the combination of the hydrolyte and the enzyme, the results above described may be construed to mean that lipase cannot form combinations with ions but only with molecules. It is interesting to note in this connection that by far the greater number of substances capable of being hydrolyzed by enzymes are, from the standpoint of the theory of electrolytic dissociation, indifferent or non-ionizable substances. These substances are so well known that they do not require mention in this connection. Only a few substances of salt type can be hydrolyzed by ferments. Such substances are potassium myronate and ammonium hippurate. To what extent these substances are ionized in aqueous solution is at present unknown to the writer if, indeed, it has ever been determined.

In view of the very thorough and exhaustive treatment which the whole subject of electrolytic dissociation has received in recent years, it would seem at first sight that quite a number of methods were available for further testing the correctness of these assumptions. Unfortunately, however, such is not the case, for, as frequently happens in investigations of this kind, the instability of the enzyme and its extreme sensitiveness to its chemical environment simply make it impossible to impose conditions which ordinarily are simple enough. Enough has already been done to make it apparent that a great many practical difficulties will have to be overcome before any additional evidence either for or against the views herein advanced is to be obtained. As soon, therefore, as the opportunity presents itself I hope to make a thorough and exhaustive study of the questions suggested by these observations.

STATE COLLEGE OF KENTUCKY,
LEXINGTON, April, 1902.

REPORTS.

Recent Work on the Derivatives of Alkali and Alkaline Earth Metals.

Within the last few years the *Comptes Rendus* has contained a number of brief articles by Moissan and his co-workers on this subject. The only long article was that published by Moissan[1] two years ago, in which he sums up his remarkable work on calcium and its derivatives. A brief report of this article was given in this JOURNAL.[2] A résumé of the many short articles seems timely. The subjects may be classed as follows : Metals, Nitrides, Derivatives of Ammonia and of Ammonium, and Hydrides.

Metals.

Beryllium.—Lebeau,[3] in 1898, obtained pure beryllium by electrolysis of beryllium-sodium fluoride, in a nickel crucible with positive graphite electrodes, the crucible acting as negative electrode. The metal was deposited as a network of crystals, which, after thorough washing with water, form a crystalline powder of white metallic luster. The metal proved to be pure. Previous attempts to prepare beryllium had been either by action of potassium or sodium on beryllium salts, or by electrolysis of the chloride or fluoride, this last method not succeeding because these salts do not conduct the current.

Barium.—Guntz,[4] working at Nancy, says that thus far no barium has been made which was proved pure by analysis. He adopts Maquenne's[5] method of starting from an amalgam containing 3 per cent barium, which is readily obtained by electrolysis of a saturated solution of barium chloride, using mercury as cathode and a platinum-iridium anode, and distilling the amalgam in a vacuum. Hitherto, barium free of mercury has not been obtained in this way, and Guntz owes his success to his method of heating. The porcelain tube was fitted into a tube of refractory earth. Platinum wire was wound about the refractory tube, protected from silica by a brasque of aluminium oxide and magnesium oxide. The whole was covered by several layers of asbestos and an electric current passed through the wire ; he could thus obtain, in a porcelain tube of 5 cm. diameter and 30 cm. length, a temperature of 1200° to 1300°, by a current of 600 to 700 Watts. Heating the tube, which contains the amalgam, very slowly, he finds that at 600° mercury

[1] Ann. chim. phys., [7], **18**, 289.
[2] This JOURNAL, **24**, 96.
[3] Compt. rend., **126**, 744.
[4] *Ibid.*, **133**, 872.
[5] Bull. soc. chim. (Paris), **7**, 386.

escapes quietly, leaving a fused amalgam in the boat. At 1000° all mercury has escaped. A higher heat volatilized the barium. It adheres to the iron boat, and in removing it with a chisel it was somewhat oxidized, as his analysis showed. Mercury and barium hydroxide were absent. Pure barium is silver-white and soft as lead ; it decomposes water and absolute alcohol. The yellow color ascribed to the alkaline earth metals by earlier observers is caused by presence of nitride.

Strontium.—Henri Gautier,[1] working in Moissan's laboratory, obtains by the action of zinc and of cadmium on strontium iodide, a zinc alloy containing 18 per cent strontium and a cadmium alloy containing 45 per cent cadmium. By heating this last alloy in a current of hydrogen at red heat he obtains strontium hydride.

Guntz,[2] in consequence of Gautier's publication, describes his incomplete work on strontium. He obtains strontium from its amalgam by the method which he used for barium, but has not yet succeeded in getting it quite free of mercury.

Nitrides.

The nitrides of barium and strontium were first isolated by the action of nitrogen on heated impure barium and strontium, and studied by Maquenne.[3] While his specimens were not quite pure, he established their chief properties and their composition, Ba_3N_2 and Sr_3N_2. The calcium nitride is described fully by Moissan[4] in his treatise on calcium. Lithium nitride was first made from impure lithium by Ouvrard[5] and its general properties noted. It may be said of the nitrides of all of these four metals that they are bronze-colored solids that burn in air, are readily acted on by chlorine, phosphorus, sulphur, and notably by water, which decomposes them quantitatively into ammonia and metal hydroxide, and by dilute acids, which give salts of the metal and ammonium.

Guntz[6] made pure lithium nitride from pure lithium, by heating it in a current of nitrogen. He confirms the composition Li_3N given by Ouvrard. He says that when heated in hydrogen the following reaction takes place :

$$Li_3N + 3H_2 = 3LiH + NH_3,$$
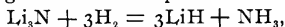
while if the hydride of lithium is heated in nitrogen this reaction is reversed :

$$3LiH + N_2 = Li_3N + NH_3.$$
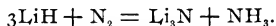
Moissan shows that this is not true of the calcium compounds,

[1] Compt. rend., **133**, 1005.
[2] *Ibid.*, **133**, 1209.
[3] Ann. chim. phys., [6], **29**, 215.
[4] *Ibid.*, [7], **18**, 289; This JOURNAL, **24**, 1.
[5] Compt. rend., **114**, 120.
[6] *Ibid.*, **123**, 995.

for calcium nitride, Ca_3N_2, heated to a red heat, yields hydride, while the reverse does not occur when the hydride is heated in nitrogen.

Metal-Ammoniums.

The fact that potassium and sodium are soluble in liquid ammonia forming blue solutions has been noticed by many chemists. Joannis was the first to make a careful study of the subject, and many articles by him are in the *Comptes Rendus* in the volumes between 109 and 117, inclusive. The date of these articles is too early to include them in this report, but it may be said that Joannis believed in the formation of unstable compounds of the composition KNH_3 and $NaNH_3$, while Seeley and other observers thought the so-called sod-ammonium and potass-ammonium to be merely solutions of the metals in liquid ammonia.

Moissan[1] has settled this question and shown that Joannis was right. To determine the temperature limit at which the substances could form, and whether, indeed, the metals would act on gaseous ammonia, he brought the metals potassium, sodium, lithium, and calcium into contact with a current of dry ammonia gas at a temperature of 100° and at atmospheric pressure. By gradually lowering the temperature he could observe the point at which the ammonia gas attacked the metals. He found that in all cases a compound was formed. The results were :

Dry ammonia gas combines with lithium at $+70°$ with liquefaction.

Dry ammonia gas combines with calcium at $+20°$ without liquefaction.

Dry ammonia gas combines with potassium at $-20°$ with liquefaction.

Dry ammonia gas combines with sodium at $-20°$ with liquefaction.

At any temperature above these the compounds break down into metal and ammonia. If the liquid compounds are kept for a time at these temperatures the excess of ammonia escapes, and the solids KNH_3, $NaNH_3$, and $LiNH_3$ remain. These, as well as the solid calcium-ammonium, $Ca(NH_3)_4$, are stable at temperatures below those given. He modified his experiments and proved that solid ammonia at $-80°$ does not act on any of these metals, but as soon as the temperature rises to the liquefaction-point of ammonia, $-75°$, the metals are attacked and all except calcium dissolve.

Common Properties of the Metal Ammoniums.—All four excepting calcium give dark-blue solutions in an excess of liquid

[1] Compt. rend., **127**, 685.

ammonia. When this excess is evaporated, bronze-colored solids remain. If any of the four metal-ammoniums are allowed to stand either in solid form or dissolved in liquid ammonia at temperatures somewhat below their decomposition temperatures, they give off hydrogen and form the metal amide

$$LiNH_3 = LiNH_2 + H.$$
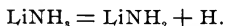
The amides of the metals are transparent crystalline substances, little soluble in liquid ammonia. The solid metal-ammoniums are all decomposed by water and take fire in the air. Further properties of this class of compounds have only been published in the articles by Joannis. Moissan promises an exhaustive article on the whole field. As to the valence of calcium in $Ca(NH_3)_4$, Moissan says: "it ·may be regarded as tetravalent, or it may be that calcium-ammonium is $Ca(NH_3)_2 + 2NH_3$." He inclines decidedly to the former view, thinking that the behavior of the substance does not warrant the latter.

Barium-Ammonium.—Guntz[1] says that barium dissolves in liquid ammonia, forming a bronze-colored liquid.

Strontium-Ammonium.—Guntz[2] says that strontium does not form this compound as readily as barium; at least liquid ammonia does not change color in contact with strontium.

Ammonium Amalgam.—Moissan[3] reviews the history of ammonium amalgam, and decides to determine the exact volumes of ammonia and of hydrogen given off in the decomposition. On account of the solubility of ammonia in water, he deemed it necessary to avoid its use, and used liquid ammonia as solvent. He first proved that sodium amalgam is not attacked by liquid ammonia at temperatures below —35°. On adding dry ammonium iodide the reaction $NH_4I + NaHg_n = NaI + NH_4Hg_n$ takes place without escape of gas, the new amalgam being more fluid. After thorough shaking, washing, and decanting with liquid ammonia to remove sodium and ammonium iodides, the amalgam is cooled to —80°, becoming very hard. After washing with ether saturated with a hydrogen at —80°, the metal is placed in a glass tube with ground-glass stopper and connected with a mercury pump. The tube is exhausted at —80° and the temperature allowed to rise slowly. At —40° the mass begins to liquefy, at —30° swells, and at +15° almost fills the tube, occupying thirty times its original volume. During this decomposition, heat is

[1] Compt. rend., **133**, 872.
[2] *Ibid.*, **133**, 1209.
[3] *Ibid.*, **133**, 803.

set free. Seven concordant analyses of the gas set free showed it to consist of two volumes of ammonia and one of hydrogen. From this work it would appear that the radical ammonium NH_4 or $(NH_4)_n$ exists in the metallic mass prepared below —35°. Moissan, however, does not believe this to be true, but thinks that a metallic hydride of ammonia is formed, which, by decomposition, causes the escape of gas.[1]

Moissan[2] has shown that when sulphur dissolves in liquid ammonia forming a dark-red liquid, this liquid contains a compound of the composition $(NH_3)_2S$, sulph-ammonium, an analogue of the metal-ammonium, which is completely dissociated at ordinary temperature and pressure. It sulphurizes in the cold a large number of elements and compounds, and it forms addition-products with ammonia.

Moissan[3] shows that lithium dissolves in methylamine forming a dark-blue solution, from which, at ordinary temperatures, ammonia escapes, till a bronze-colored solid, $LiNH_2CH_3$, remains, which is stable at ordinary temperature.

Attempts to isolate the Ammonium Radical.—Moissan has attacked this problem in different ways. In one artiticle,[4] referring to the work of O. Ruff[5] on the electrolysis of ammonium iodide in solution in liquid ammonia, he describes similar results with ammonium chloride at —75°, finding that hydrogen and chlorine escape at the poles, no nitrogen escaping. Hence the group NH_4 is unstable at —75°. He found the same results with ammonium iodide at —75°, while Hugot[6] finds that free iodine acts on liquid ammonia at —33°.5, forming the compound $NI_3,3NH_3$.

Moissan[7] studies the action of ammonium chloride on lithium-ammonium and calcium-ammonium dissolved in liquid ammonia at —75°. There were two possibilities :

I. $Ca(NH_3)_4 + 2NH_4Cl = CaCl_2 + 4NH_3 + 2NH_4$;

II. $Ca(NH_3)_4 + 2NH_4Cl = CaCl_2 + 6NH_3 + 2H.$
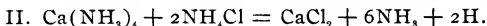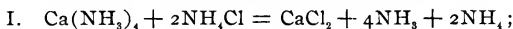
Both with calcium-ammonium and lithium-ammonium the reaction was as represented in equation II. The experimental details are very striking.

Moissan[8] tries the action of dry liquid hydrogen sulphide

1 Moissan seems to consider NH_4 not as a metallic radical "ammonium" but rather as a metallic-ammonia hydride, or hydrogen-ammonium, in which case it belongs to one of these two series : NaH, KH, LiH, NH_3H, or KNH_3, $NaNH_3$, $LiNH_3$, HNH_3.
2 Compt. rend., **132**, 510.
3 *Ibid.*, **128**, 26.
4 *Ibid.*, **133**, 713.
5 Ber. d. chem. Ges., **34**, 2604.
6 Ann. chim. phys., [7], **21**, 23.
7 Compt. rend., **133**, 715.
8 *Ibid.*, **133**, 771.

on the ammonium metals, as it might be possible that the reaction, $2(LiNH_3) + H_2S = Li_2S + 2NH_4$, might occur at low temperature. As a matter of fact ammonia and hydrogen are given off at $-73°$. In this experiment too, the beauty and ingenuity of the experimental work command admiration. Moissan concludes the article with these words: "Ammonium, which, in fact, only represents a theoretical conception intended to unify some formulas, does not seem to exist at $-73°$ in the presence of liquid hydrogen sulphide."

Hydrides.

Until recently little was known of compounds of the alkali and alkaline earth metals with hydrogen. Hautefeuille and Troost, in 1874, studied the action of hydrogen on potassium and sodium, and found that these metals absorb hydrogen as does palladium, and that substances of metallic appearance are formed to which they assigned the composition K_2H and Na_2H. Winkler, in 1891, studied the action of magnesium on oxides of calcium, barium, and strontium, heated in a current of hydrogen, and believed, from the behavior of the resulting mixtures toward water, that hydrides of barium, strontium, and calcium were formed of the general composition, MeH. The univalence of these metals corresponding with the semivalence—if this term can be used—in the hydrides of sodium and potassium, Me_2H.

The first ray of light on this subject came from the fine work of Guntz on lithium and its derivatives. In an article[1] on lithium hydride he confirms Troost and Hautefeuille's observation that below red heat lithium absorbs seventeen times its volume of hydrogen without changing appearance ; but he finds that if lithium is heated rapidly to a bright-red in an iron boat, in a current of hydrogen, it takes fire and burns, forming a fused, very hard, white mass, which analysis proved to be lithium hydride of the composition LiH. The fused hydride is not deliquescent ; is scarcely attacked by cold air ; heated in air it gives $LiO + H_2O$; it decomposes water, $LiH + H_2O = LiOH + H_2$. Heated in nitrogen it yields nitride and ammonia. The subject was not further investigated until 1890, when Moissan[2] made calcium hydride from pure calcium. It is much more active than lithium hydride. Its properties were very carefully studied. It has been already described in this JOURNAL.

Barium hydride was made in 1891, by Guntz,[3] by heating

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[1] Compt. rend., **122**, 244.
[2] *Ibid.*, **127**, 29; Ann. chim. phys., [7], **18**, 289; This JOURNAL, **24**, 96.
[3] Compt. rend., **132**, 963.

barium amalgam in a current of hydrogen at 1200°. It is a grayish-white, fused, crystalline mass of the composition BaH_2. It was not quite pure, as he found it impossible to remove traces of mercury and of iron from the boat. When heated in nitrogen it decomposes at bright-red heat, forming nitride, as does the hydride of lithium, while calcium hydride is not attacked by nitrogen.

Strontium hydride was first made by Gautier[1] in 1901. The announcement was brief. Two weeks later Guntz[2] published his unfinished work on strontium and its hydride, which he obtained from strontium amalgam, but as yet quite impure. Two weeks after this Gautier published another article[3] in which he describes pure strontium hydride ; he obtained it from a cadmium-strontium alloy, by heating very slowly in a magnesia boat, in a porcelain tube in a current of dry, pure hydrogen. The hydride was a white fused solid. Its reactions are similar to those of calcium hydride.

Potassium Hydride.—Moissan[4] recently made potassium hydride by heating potassium in a current of dry hydrogen in an iron boat in a glass tube, so that the under side of the tube is at 360°, while the upper side is cooler. The hydride sublimes and condenses as a tangled mass of snow-white crystals on the cooler side of the tube. When enough has collected the tube is cooled in a current of hydrogen, the boat slid back, and the part of the tube containing the hydride fused at both ends. Thus a tube of hydride is needed for every experiment, as it is so reactive that it can scarce be removed from the tube. It decomposes water, takes fire in cold oxygen, cold air, cold fluorine, and in cold chlorine. It is a violent reducing agent. It does not act on liquid ammonia, but if heated with gaseous ammonia yields amide, $KH + NH_3 = KNH_2 + H_2$. Analyses prove the absolute purity of the hydride.

He[5] makes potassium formate quantitatively by union of potassium hydride and carbon dioxide at ordinary temperature. He[6] makes ethane and methane quantitatively, by action of potassium hydride on ethyl iodide and on methyl chloride.

Sodium Hydride.—Moissan[7] made sodium hydride in the same way as the potassium hydride, which it resembles in appearance and reactions. The best temperature is 360°. He finds that if the boat be kept for some time at 360° the sodium

[1] Compt. rend., **133**, 1005.
[2] *Ibid.*, **133**, 1209.
[3] *Ibid.*, **134**, 100.
[4] *Ibid.*, **134**, 18.
[5] *Ibid.*, **134**, 261.
[6] *Ibid.*, **134**, 389.
[7] *Ibid.*, **134**, 71.

in the boat absorbs and dissolves some of the hydride, for if the sodium is dissolved in liquid ammonia a white substance remains undissolved which proves to be the hydride, though never quite pure, as in spite of all precautions it always contains traces of sodium oxide. Obtained by the sublimation method it is quite pure. 　　　　　　　　　　　E. RENOUF.

A New Method for the Preparation of Unsaturated Hydrocarbons.

In recent numbers of the *Berichte*[1] W. Ipatiew describes the results of a study of the pyrogenetic decomposition of alcohols. When the vapor of the alcohol was passed through tubes heated in a combustion furnace it was decomposed, the products depending upon the nature of the tube or the foreign substance placed in it. The decompositions can be expressed by the following equations:

$$(1)\ C_2H_5OH = C_2H_4 + H_2O\ ;$$
$$(2)\ C_2H_5OH = CH_3COH + H_2.$$
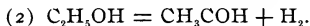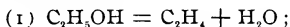
If a glass or iron tube was used the amount of the unsaturated hydrocarbon formed was small. The introduction of stick zinc into the tube caused a considerable increase in the amount of aldehyde formed, amounting in some cases to a yield of 80 per cent. When, on the other hand, powdered zinc was used the yield of hydrocarbon was increased.

This suggested the possibility of securing some substance which would influence the reaction as much in favor of the formation of the hydrocarbon as stick zinc does in favor of the aldehyde.

Experiment showed that impure graphite, such as is used for crucibles, would give the desired results. If the vapor of the alcohol was passed through a glass tube containing the scraps of broken crucibles, which were heated to 600°, an energetic decomposition took place with the formation of the hydrocarbon and water. The results obtained in several experiments will give an idea of the yield. One hundred and fifty grams of ethyl alcohol were passed through the tube in thirty minutes and about half of the alcohol was decomposed. The ethylene was absorbed in bromine and 160 grams of pure ethylene bromide was obtained. Only about 1 gram of aldehyde was formed. In another experiment 127 grams of propyl alcohol was used, and in an equal time 160 grams of propylene bromide was obtained.

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[1] Ber. d. chem. Ges., **34**, 3579 (1901); **35**, 1047 (1902).

Other alcohols acted in a similar manner showing the method to be a general one. The apparatus is quite simple, and if the temperature can be regulated there should be no difficulty in obtaining large amounts of the gases, as the graphite lasts for a long time and the process is a continuous one.   J. ELLIOTT GILPIN.

Barium Sulphate in Gravimetric Analysis.

" The exact determination of sulphuric acid as barium sulphate in no sense belongs among the simple and easy tasks as was early supposed, but requires great attention and great care."[1] In fact, the studies made before and since this became generally recognized (and which will be covered by this review) prove the extreme difficulty, if not impossibility, of precipitating barium sulphate pure.

The analytical value of barium sulphate was recognized very early, possibly first about 1750, by Bergmann,[2] and to this is likely due the fact that its composition received attention from Vauquelin,[3] Kirwan and Klaproth,[4] Aiken,[5] Berard,[6] Berzelius,[7] and others[8] prominent among the founders of quantitative analysis.

The ease with which it carries down with it salts and acids, of themselves soluble in water, and the difficulty of entirely removing these even by digestion with strong acids, are characteristic of it. " The precipitate produced in a solution containing sulphuric acid or sulphates by barium salts is never perfectly pure barium sulphate,"[9] and the "impurities are in a state of combination which cannot be broken up by an excess of acid."[10]

Records of difficulties due to the presence of various salts and acids exist in considerable number. Those due to magnesium salts and salts of weak bases, such as iron and copper, were discovered by Berzelius,[11] those due to alkaline sulphates by Turner,[12] to barium nitrate by E. Mitscherlich,[13] to

1 Fresenius: Anleit. zur Quant. Chem. Anal., 6 Aufl., **1**, 391.
2 Fourcroy's Chemistry, Heron's translation from 4th French edition, Vol. I., 321.
3 Ann. chim. phys., [1], **50**, 168 (1804).
4 J. für Chem. und Phys. (Gehlen), **5**, 515 (1805).
5 Nicholson's Jour., **22**, 304.
6 Ann. chim. phys., [1], **71**, 69 (1809).
7 *Ibid.*, [1], **78**, 30 (1811).
8 Fourcroy, Thenard, Richter, and Buchholz.
9 H. Rose: Handb. Anal. Chem., 6th Ed., II., pp. 24, 25, 455 (1871).
10 Berzelius: Ann. chim. phys., [2], **14**, 376 (1820).
11 *Loc. cit.*; compare Fresenius: Ztschr. anal. Chem., **19**, 53 (1880); Jannasch: J. prakt. Chem., **147**, 333, foot-note (1889); Lunge: Ztschr. anal. Chem., **19**, 419; Gladding: J. Am. Chem. Soc., **17**, 398.
12 Phil. Trans., **1**, 291 (1829); Compare Berzelius: Jahresbericht, 1831, p. 142; also discussion between Berzelius and Thomas Thomson; Jahresbericht, 1827, p. 77; Phil. Mag., (2), **4**, 453 (1828); *Ibid.*, (2), **5**, 221 (1829).
13 Pogg. Ann., **55**, 209 (1842).

cerium salts by Marignac,[1] to barium chloride by E. Siegle,[2] to potassium chloride (and chlorate) by H. Rose,[3] to aluminium salts by A. Mitscherlich,[4] to platinum salts by Claus,[5] to lithium salts by K. Diehl,[6] to alkaline chlorates and nitrates by Fresenius,[7] to mixtures of alkaline chlorides and sulphates by Kretschy,[8] to ammonium and sodium sulphates and to vanadium compounds by H. Rose,[9] to potassium chloride by B. Schultze,[10] to zinc chloride by Jannasch and Richards,[11] to sulphuric acid by H. Rose,[12] to phosphoric acid by Scheerer and Rube[13] and by Spiller,[14] to organic acids by Jannasch and Richards.[15]

Substances are known that inhibit the precipitation. Chromium salts[16] may entirely prevent it, and ferric salts in hot solutions[17] behave in an analogous way, but quite feebly. Tartaric and racemic acids restrain it slightly, and alkaline citrates[18] very markedly. Nitric acid[19] (under certain peculiar conditions), and metaphosphoric[20] and metaboric[21] acids interfere similarly.

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[1] Arch. des Sc. phys. et nat., **8**, 265; also Ann. Chem. (Liebig), **68**, 216 (1848).

[2] J. prakt. Chem., **69**, 142 (1856). Compare H. Rose: Pogg. Ann., **113**, 627 (1861); Mar : Am. J. Sci., [3], **41**, 288 (1891); Browning: *Ibid.*, [3], **45**, 403 (1893); Phinney: *Ibid.*, [3], **45**, 471 (1893). The last three articles illustrate admirably how one may be misled by errors from this source. Richards and Parker : Ztschr. anorg. Chem.. **8**, 413 (1895). This article sets forth the results of a careful study of the difficulties and the best way of dealing with them.

[3] Pogg. Ann., **113**, 627 (1861).

[4] J. prakt. Chem., **83**, 455 (1861).

[5] *Ibid.*, **85**, 129 (1862); also Jahresbericht, 1861, p. 323.

[6] Ann. Chem. (Liebig), **121**, 98 (1862).

[7] Ztschr. anal. Chem., **9**, 52 (1870); compare Gladding : J. Am. Chem. Soc., **16**, 398 (1894).

[8] Ztschr. anal. Chem., **10**, 396 (1871).

[9] Handb. Anal. Chem., 6th Ed., II., pp. 368, 456 (1871).

[10] Wagner's Jahresbericht, 1882, p. 264.

[11] J. prakt. Chem., **147**, 321 (1889); compare Thiel : Ztschr. anorg. Chem., **22**, 424 (1900).

[12] Handb. Anal. Chem., 6th Ed., II., p. 455 (1871).

[13] J. prakt. Chem.. **75**, 113 (1858).

[14] Chem. News, **10**, 219; also Jahresbericht, 1864, p. 695.

[15] J. prakt. Chem., **147**, 325 (1889); compare Spiller : J. Chem. Soc. (London), **10**, 110 (1858); Gladding : J. Am. Chem. Soc., **16**, 398; Küster and Thiel : Ztschr. anorg. Chem., **19**, 101 (1899).

[16] Recoura : Ann. chim. phys., [7] **4**, 494; Whitney : Ztschr. phys. Chem., **20**, 40.

[17] Fresenius : Ztschr. anal. Chem., **19**, 53 (1880); Lunge: *Ibid.*, **19**, 419 (1880); Gladding : J. Am. Chem. Soc., **16**, 398 (1894); compare Ostwald : Ztschr. phys. Chem., **29**, 340.

[18] Spiller : J. Chem. Soc. (London), **10**, 110 (1858).

[19] E. Schöne : Pogg. Ann., **112**, 214.

[20] Metaphosphoric acid calls for a more detailed consideration. Recently, Wiesler (Ztschr. anorg. Chem., **28**, 198 (1901)) called attention to the fact that he had no difficulty in analyzing barium metaphosphate, whereas Graham had stated that this acid partly prevents the precipitation of barium as sulphate. The reviewer has not yet found this statement in Graham's papers; in his well-known article read before the Royal Society two analyses of barium metaphosphate are described, but both yielded precipitates that were too heavy (Phil. Trans., 1833, pp. 253 to 284; also Pogg. Ann., **32**, 69 (1834); and Alembic Club Reprints, No. 10). The statements to be found in the text-books regarding this matter (Fresenius : Anleit. zur. Quant. Anal., 6th Ed., I., p. 152; H. Rose : Handb. Anal. Chem., 6th Ed., II., p. 555; Menschutkin: Anal. Chem. (trans. by Locke), 309) are based upon the experiments of Scheerer and Rube (J. prakt. Chem., **75**, 113 (1858)) which clearly showed the difficulty of complete precipitation in the presence of metaphosphoric acid; this was confirmed by Spiller's work (Chem. News, **10**, 219 (1864)). It might be suggested in explanation

In these cases there is more or less reason for the belief in the formation of double salts, or of "complexes" in the solutions, in which compounds the barium or the sulphuric acid, or both, are involved.

If it is possible to distinguish between such cases and those where other substances in solution (in some simpler way, perhaps) merely increase the solubility of the barium sulphate, we can distinguish a third class of substances whose presence, at least in any considerable amount, is to be avoided where barium sulphate is to be precipitated. Nitric[1] and hydrochloric acid,[2] alkaline[3] and ammonium nitrates[4] belong here. Under the conditions of most analyses, however, barium sulphate is very insoluble;[5] so, also, in water.[6]

In order to precipitate barium sulphate quantitatively, and in a form easily filtered and washed, and at the same time least impure, it is best to have the solutions which are to be mixed dilute[7] and hot,[8] to mix them very slowly and with constant stirring,[9] and to have the precipitant present in con-

that probably Wiesler had converted all of his meta acid into the ortho acid before the precipitation of barium sulphate was made, for Spiller found orthophosphoric acid to have no such influence. But Scheerer and Rube's statement that the precipitates formed in solutions containing metaphosphoric acid do not contain it, but the ortho acid, is confusing to this explanation. A second suggestion of an explanation arises from the fact that Wiesler was analyzing a trimetaphosphate, whereas the others referred to were analyzing hexametaphosphates. Further, while Maddrell (Ann. Chem. (Liebig), **61**, 53 (1847)) mentions no difficulty in analyzing barium dimetaphosphate by heating with concentrated sulphuric acid, Ludert (Ztschr. anorg. Chem., **5**, 33 (1894)) obtained rather unsatisfactory results when he applied the same method to hexametaphosphates. If Fleitmann experienced difficulties in the analyses of barium metaborates, he avoided them by digesting the finely ground salt with a solution of sodium carbonate (Pogg. Ann., **78**, 361 (1849)).

²¹ Horn : Dissertation, p. 52 (1900).

1 and ² Piria : Il Cimento, anno V., p. 257 (1847) ; H. Rose : Pogg. Ann., **95**, 109 (1855) ; Calvert : Chem. Gaz., 1856, p. 55 ; also Phil. Mag., [4], **11**, 390 (1856) ; Nicholson and Price : Phil. Mag., [4], **11**, 169 (1856) ; Noad ; J. Chem. Soc. (London), **9**, 15 (1857) ; Siegle : J. prakt. Chem., **69**, 142 (1856) ; Gatkowsky : Ber. d. chem. Ges., **5**, 330 ; Erdmann and Mittenzwey : J. prakt. Chem., **75**, 214 (1858) ; Gladding : J. Am. Chem. Soc., **16**, 398 (1895).

³ Fresenius : Ztschr. anal. Chem., **9**, 52 (1870).

⁴ Erdmann and Mittenzwey : *Loc. cit.*

⁵ Fresenius : *Loc. cit.* One part requires for its solution 400,000 parts of water. Fresenius (Ztschr. anal. Chem., **30**, 455 (1891)) carefully repeated his work and found one part required for its solution 401,000 parts of water (containing 1.1 per cent hydrochloric acid and 0.46 per cent sulphuric acid).

⁶ Marqueritte (Compt. rend., **38**, 308 (1854)) had placed the solubility at 1 part in 200,000 parts of water, while Calvert (*Loc. cit.*) placed it at 1 part in 800,000 parts of water. Calculated from electrical conductivity experiments, its solubility in water is 1 part in 429,700 parts of water at 18°.4 C., or 1 part in 320,000 parts of water at 37°.7 C., according to Holleman (Ztschr. phys. Chem., **12**, 131 (1893)). One part dissolves in 436,030 parts of water at 19° C., according to Kohlrausch and Rose (Ztschr. phys. Chem., **12**, 241 (1893)).

⁷ Bunsen (Ztschr. anal. Chem., **10**, 396 (1871)) recommended that each 100 cc. yield 0.1 gram of barium sulphate. H. Rose : Handb. Anal. Chem., II., p. 454 (1871) ; the precipitate runs through the filter when precipitated from concentrated solutions. Richards and Parker : Ztschr. anorg. Chem., **8**, 421 ; the more dilute the solution the less barium chloride is enclosed by the precipitated sulphate.

⁸ H. Rose : Handb. Anal. Chem., II., p. 455; the precipitate is purer when formed in hot solutions than in those at ordinary temperatures. Menschutkin : Anal. Chem. (trans. by Locke), p. 39 ; the precipitate is amorphous and runs through the filter when it has been formed in cold solutions.

⁹ H. Rose : *Loc. cit.*, p. 454. Richards and Parker : *Loc. cit.*, p. 421 ; the precipitates enclose more barium chloride when the solutions are mixed quickly.

siderable excess[1] in the resulting mixture. The solution of the
barium salt should always be added to that of the sulphate or
sulphuric acid, and if it is permitted to flow down the wall of
the beaker in which the sulphate solution is contained, and
thus meet the latter in a broad, thin film, the precipitate is
less impure than if the solution be added drop by drop.[2] It is
customary to have present some[3] hydrochloric acid to aid in
converting the precipitate entirely to the crystalline form.[4]

It is usual also to digest the mixture some time over a low
flame,[5] and to filter only after the mixture has become cold.[6]

Various methods for removing the substances which barium
sulphate has carried down with it have been suggested.
Treatment with hydrochloric acid was tried and abandoned by
Berzelius[7] as inefficient, and it has succeeded little better in
the hands of other chemists.[8] Brügelmann,[9] however, recom-
mends it as an aid in partially overcoming the errors due to
enclosed substances. Solution of the impure precipitates in
concentrated sulphuric acid, and reprecipitation by diluting
these solutions was advised by A. Mitscherlich,[10] but it is
self-evident that such a procedure is useless where barium
salts constitute all or part of the impurity;[11] yet this method

[1] Berzelius: Lehrb. der Chemie, III., p. 105; when solutions containing equivalents
of barium chloride and potassium sulphate are mixed, 2.25 per cent of the barium
used remains unprecipitated. Compare Note 12, p. 495, of this report. Joulin: Ann.
chim. phys., [4], **30**, 274; when solutions containing barium chloride and sodium
sulphate at N/5000 dilution are mixed, 1/27 of the salts remain undecomposed after
twenty-four hours; only after four days is the precipitation complete. H. Rose:
Loc. cit.; an excess of barium salt hastens complete precipitation. Richards and
Parker: *Loc. cit.*, p. 419; an excess of barium chloride diminishes the solubility of
the precipitate and does not increase the amount of barium chloride enclosed.
[2] Richards and Parker: *Loc. cit.*, p. 420; otherwise the quantity of barium chlo-
ride carried down is greater. H. Rose: *Loc. cit.*, p. 455; if the sulphate separates in
a liquid which contains no barium chloride in excess it is almost free from barium
chloride. Compare with the following, where the reverse order is followed and
recommended: Mar, Browning, and Phinney, Note 2, page 496 of this report. Their
precipitates contained barium salts as impurities, because when "purified" by solu-
tion in concentrated sulphuric acid and reprecipitation they weighed more than be-
fore. Mar explained this as due to "residual contamination."
[3] Fresenius: Ztschr. anal. Chem., **9**, 52 (1870); if much hydrochloric acid is pres-
ent it must be removed by evaporation, because it has great solvent action on barium
sulphate. Richards and Parker: *Loc. cit.*, p. 420; the presence of much free hydro-
chloric acid "enormously" increases the amount of barium chloride enclosed.
[4] Ostwald: Scientific Foundations of Analytical Chemistry (trans. by Mc-
Gowan), **22**, 197.
[5] Richards and Parker: *Loc. cit.*, p. 416; "about an hour."
[6] Compare Note 6, p. 497, of this report.
[7] *Loc. cit.*, Note 10. p. 495, of this report.
[8] H. Rose: *Loc. cit.*, p. 455; treatment with hydrochloric acid is "useless."
[9] Ztschr. anal. Chem., **16**, 22; after heating in a crucible the precipitate is
treated with 3 or 4 drops of moderately strong hydrochloric acid, the lumps of the
precipitate being broken up with a glass rod and the mixture warmed two minutes
without boiling, over a gas-flame. The solution obtained is poured through a small
filter and then the whole operation repeated several times until the filtered liquid
remains clear when tested with sulphuric acid. Then the entire precipitate is
brought upon the filter, washed with boiling water, dried, heated, and weighed.
[10] J. prakt. Chem., **83**, 458 (1861).
[11] This was pointed out at the time; see Jahresbericht, 1861, p. 845, foot-note;
also later by Fresenius: Ztschr. anal. Chem., **9**, 52 (1870). Compare Richards and
Parker: *Loc. cit.*, p. 413; also Mar, Phinney, and Browning: *Loc. cit.*

removes alkali salts so completely that the spectroscope fails to detect more than the merest traces of them.[1]

Digestion with an acetic acid solution of copper acetate, though recommended,[2] is also useless.[3] Barium sulphate can be freed from many substances by fusion with four or more times its mass of alkaline carbonates,[4] whereby the barium is completely converted to carbonate, which can be filtered off, washed, and dried, and weighed as such or converted into sulphate.

After a precipitate of barium sulphate has been washed and dried, a quite usual practice[5] is to remove the precipitate as completely as possible from the filter-paper upon which it was collected to a weighed crucible, and then to burn the paper on a platinum wire held over the crucible. Reduction may occur even then to a greater or less extent,[6] and if the paper be burned in the crucible the percentage of reduction may become very great.[7] Richards,[8] however, has found that if the crucible be kept at such a temperature that the paper completely chars without bursting into flame, no considerable reduction takes place then or in the subsequent burning out of the charred paper. If reduction occurs, the barium sulphide may be reconverted to sulphate by heating the precipitate in an open, tilted crucible, or by the addition of a drop of concentrated sulphuric acid,[9] and subsequent removal of the excess of the same by heating to constant weight.

Barium sulphate cannot be heated with safety above a dull-

[1] H. Rose : *Loc. cit.*, p. 27.
[2] Stolba : Ding. poly. J., **168**, 431 ; also Ztschr. anal. Chem., **2**, 390 (1863).
[3] Fresenius : Ztschr. anal. Chem., **9**, 52 (1870). H. Rose : Handb. Anal. Chem., II., p. 455.
[4] H. Rose : Pogg. Ann., **95**, 96. It is necessary to use from six to seven times the equivalent weight of potassium carbonate to insure complete conversion of the barium sulphate to carbonate. But six to seven times the equivalent weight of sodium carbonate does not give complete decomposition of the sulphate even after one and a half hours. However, on account of the lower molecular weight of the sodium carbonate, four times the mass of either carbonate is sufficient. The origin of the fusion method in analytical operations and its application to barium sulphate is not without interest, if only historical. Scheele, who discovered that heavy spar is barium sulphate, was unacquainted with the fusion method, and decomposed the mineral by heating with charcoal or honey (Scheele's Werke, II., p. 179). Marggraf is the first to record the use of an alkaline carbonate in analysis by fusion ; he used potassium carbonate to decompose "Bologne stone" (Marggraf's Chemische Schriften, Berlin, 1767, II., p. 135). Wiegleb was the first to recommend Marggraf's method for barium sulphate, but because he used only one and a half times the equivalent weight of potassium carbonate to one of barium sulphate, the decompositions were never complete (Crell: Neueste Entdeckungen in der Chemie, II., p. 14). Stromeyer later applied it to heavy spar (Stromeyer's Untersuchungen, p. 222). H. Rose (*Loc. cit.*) was the first to carefully work out the proper mass relations for complete decomposition.
[5] Fresenius : Ztschr. anal. Chem., **16**, 339.
[6] Hagar : "Untersuchungen," 2d Ed., I., p. 711.
[7] C. W. Marsh : J. Anal. Chem., **3**, 164 (1889). There may be from 2 to 22 per cent of the barium sulphate reduced, depending upon conditions.
[8] Ztschr. anorg. Chem., **8**, 417 (1895).
[9] Marsh (*loc. cit.*) suggested sulphuric acid as an improvement on Hagar's prior suggestion of nitric acid, because barium sulphide evolves sulphuretted hydrogen when treated with acids.

red heat. Over a blast-lamp it will lose in weight as much as 1 per cent in thirty-five minutes. It is then alkaline in reaction, the loss having been due to the escape of sulphur trioxide.[1]

<div align="right">D. W. HORN.</div>

Gravimetric Determination of Sulphuric Acid in the Presence of Iron.

The precipitation of barium sulphate, quantitatively and in a pure form, is probably no where else of so great industrial importance as in the analysis of pyrites. The fact that iron salts interfere at times, if not always, in such analyses is a matter of great significance to those concerned therein, and one of interest to all chemists as a special, and probably the best known case of "occlusion" of impurities by a precipitate. Berzelius first observed this fact and was of the opinion (which it is believed this report confirms) that "it is necessary to begin by removing the oxide"[2] (of iron).

Four different ways of avoiding the difficulties incident to such analyses find expression in the methods which are recommended in the literature :

1. The separation of the iron and sulphur by fusion with some oxidizing flux.

2. The separation of the iron as hydroxide, by means of ammonium hydroxide, from the solution in which the sulphuric acid is to be determined.

3. The reduction of the iron in the solution to the ferrous condition, before precipitating the barium sulphate.

4. The retention of the iron in the solution by the addition of organic acids before the precipitation.

The first principle is involved in the Fresenius method,[3] by which the pyrites are fused[4] with a mixture of potassium nitrate and alkaline carbonates, and the sulphuric acid determined in the filtrate obtained by extracting the melt with cold water after removing from it all nitric acid. The method has been repeatedly tested[5] and seems to have become the criterion by which other methods are judged.

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[1] Boussingault: Compt. rend., **64**, 1159 (1867) ; Ztschr. anal. Chem., **7**, 244 ; compare Bunsen : Ann. Chem. (Liebig), **111**, 262 (1859).
[2] Ann. chim. phys., [2], **14**, 376 (1820).
[3] Ztschr. anal. Chem., **16**, 339 (1877) ; also Fresenius : Anleit. zur Quant. Anal., 6th Ed., II., p. 453 (1896).
[4] Other reagents for decomposition have been recommended : Lime and soda, by Hayes : Amer. Chemist, **5**, 271 ; caustic potash and bromine water, by Iles : Ber. d. chem. Ges., **11**, 1187 ; soda and magnesia, by Clark : J. Soc. Chem. Ind., 1885, p. 329.
[5] Fresenius : *Loc. cit.* ; Ztschr. anal. Chem., **19**, 53 (1880) ; Lunge : *Ibid.*, **19**, 419 ; Jannasch and Richards : J. prakt. Chem., **147**, 333 (1889). "For the exact analysis of pyrites, Fresenius' method of fusion, as our experiments indicate, is the best and only correct method." Lunge and Obregia : J. prakt. Chem., **148**, 241 (1889) ; Ztschr. angew. Chem., 1889, 476. Gladding : J. Am. Chem. Soc., **16**, 401 (1894) ; Chem. News, **70**, 182 (1894). Lunge and Misslin : Ztschr. anorg. Chem., **21**, 198 (1899).

It has been criticized as troublesome and tedious.[1] Further, the oxidizing flux attacks the crucible and the dissolved platinum may interfere with the subsequent iron determination,[2] and where coal gas is used in the burner over which the fusion is accomplished, the sulphur it contains may give rise to considerable errors.[3]

Lunge devised a method involving the second principle already mentioned. The original Lunge method[4] consisted in dissolving[5] the pyrites in aqua regia, evaporating this solution repeatedly with hydrochloric acid to get rid of nitric acid,[6] diluting the residue, and determining the sulphuric acid in this solution as usual. But the barium sulphate precipitates thus obtained are always rendered impure by the presence of iron compounds,[7] and weigh too much or too little, according to the heat to which they are subjected before weighing.[8] To avoid this, Lunge modified[9] his method, introducing the precipitation of the iron as hydroxide by ammonium hydroxide and determining the sulphuric acid in the filtrate therefrom. One can obtain excellent results by this modified "Lunge method," but many analysts have experienced difficulties in so doing, on account of the formation and retention of some basic iron sulphate in the ferric hydroxide precipitate. As a result of this, the method has often been condemned and as often vindicated.[10]

Because of this difficulty and to do away with the tedious washing of the ferric hydroxide, Gladding modified the "Lunge method" in that he directed, instead of washing out all sulphuric acid from the ferric hydroxide, to dissolve the precipitate in hydrochloric acid and then add barium chloride, collecting the sulphate obtained on the same paper as

[1] Lunge: "Sulphuric Acid and Alkali," I., p. 55; Ztschr. anal. Chem., 19, 419; Gladding: J. Am. Chem. Soc., 16, 399 (1894) ; Chem. News, 70, 182.
[2] Jannasch : J. prakt. Chem., 147, 334 (1889).
[3] Price : Ztschr. anal. Chem., 3, 483 (1864).
[4] "Handb. der Soda Indus.," I., p. 96.
[5] Other solvents have been recommended : Fuming nitric acid, Fresenius : "Sulphuric Acid and Alkali," I., p. 52; nitric acid and bromine, Gladding : J. Am. Chem. Soc., 16, 398 (1894) ; Chem. News, 70, 181; see also Lunge: J. Am. Chem. Soc., 17, 181 (1895) ; Chem. News, 71, 132; and Gladding : J. Am. Chem. Soc., 17, 397 (1895). Caustic soda solution and bromine, Drown : Chem. News, 43, 89 (1881).
[6] Compare Fresenius : Ztschr. anal. Chem., 9, 52 (1870).
[7] Fresenius : Ztschr. anal. Chem., 19, 53 (1880) ; compare Lunge : *Ibid.*, 19, 419.
[8] Jannasch and Richards : J. prakt. Chem., 147, 321 (1889).
[9] Lunge : Ztschr. anal. Chem., 19, 419 (1880).
[10] Jannasch and Richards : J. prakt. Chem., 147, 333 (1889) ; *Ibid.*, 148, 236 (1889). Lunge, Barbezat, and Obregia : *Ibid.*, 148, 239 ; Ztschr. angew. Chem., 1889, p. 473. Gladding : J. Am. Chem. Soc., 16, 398 (1894) ; Chem. News, 70, 181. Lunge: J. Am. Chem. Soc., 17, 181 (1895) ; Chem. News, 71, 132. Gladding : J. Am. Chem. Soc., 17, 397. Lunge : *Ibid.*, 17, 772 (1895) ; Ztschr. anorg. Chem., 19, 454 (1899). Lunge and Misslin : *Ibid.*, 21, 198 (1899). Meineke : Ztschr. anal. Chem., 38, 215 ; *Ibid.*, 38, 351. Lunge and Bebie : Ztschr. anorg. Chem., 21, 200; Pattinson : J. Soc. Chem. Ind., 1885, p. 329 ; *Ibid.*, 1890, p. 21.

that used in the first filtration. Lunge protested vigorously.[1]

The "Gladding modification" as such has probably never come into general use, but is now used in a form proposed by Küster and Thiel, which consists in omitting the collection of the ferric hydroxide on a filter, but dissolving it, as did Gladding, with hydrochloric acid after an excess of barium chloride has been added to the ammoniacal solution from which the iron was precipitated, but in which it is still suspended. This method has come through numerous tests and attacks.[2]

The idea of reducing the iron to the ferrous condition originated with Jannasch and Richards, in an analogy to titanic acid.[3] It seemed possible that ferrous salts would not be carried down by barium sulphate as were ferric salts. But after trying this plan, using zinc and hydrochloric acid[4] for the reduction, they abandoned it because the precipitates still contained not only iron, but also zinc compounds. A detailed study by Thiel[5] confirms this and indicates a further difficulty arising from the excess of zinc retaining some of the sulphuric acid. On the other hand, Heidenreich,[6] Meineke,[7] and Lunge and Bebie[8] have gotten excellent results by this method. The explanation of this apparent contradiction will only become apparent, probably, when not results alone but also experimental details are published by those who use this method successfully.

The fourth and last method was likewise applied first by Jannasch and Richards.[9] The organic acids[10] they used to "keep up" the iron were formic, acetic, and citric, but, nevertheless, the barium sulphate precipitates contained iron. Later, Gladding[11] tried and abandoned this plan, using citric acid. Küster and Thiel[12] used oxalic and tartaric acids with

[1] Gladding : J. Am. Chem. Soc., **16**, 401, 404 ; Chem. News, **70**, 182 (1894). Lunge : J. Am. Chem. Soc., **17**, 181 ; Chem. News, **71**, 132. Lunge and von Keler : J. Am. Chem. Soc., **17**, 183-186 ; also Ztschr. angew. Chem., 1895, pp. 71, 72. Gladding : J. Am. Chem. Soc., **17**, 399 (1895). Lunge : *Ibid.*, **17**, 775 (1895).
[2] Küster and Thiel : Ztschr. anorg. Chem., **19**, 98 (1899). Lunge . *Ibid.*, **19**, 455 (1899). Küster and Thiel : *Ibid.*, **21**, 73 (1899). Lunge and Misslin : *Ibid.*, **21**, 198 (1899). Meineke : Ztschr. anal. Chem., **38**, 209, 215 ; *Ibid.*, **38**, 351. Lunge and Bebie : Ztschr. anorg. Chem., **21**, 200 (1899).
[3] J. prakt. Chem., **147**, 322 (1889).
[4] Jannasch and Richards used other reducing agents also : metallic aluminium, metallic magnesium, and sodium amalgam. But the precipitates were always impure. Since then Johnson (Chem. News, **70**, 212 (1894)) proposed sodium hypophosphite as the reducing agent, but Lunge (J. Am. Chem. Soc., **17**, 187) has shown that Johnson's claims for this method are not borne out by experiment.
[5] Ztschr. anorg. Chem., **22**, 441 (1900).
[6] *Ibid.*, **20**, 233 (1899).
[7] Ztschr. anal. Chem., **38**, 209, 351 (1899).
[8] Ztschr. anorg. Chem., **21**, 200 (1899).
[9] J. prakt. Chem., **147**, 325 (1889).
[10] Some organic acids prevent complete precipitation. Spiller : J. Chem. Soc. (London), **10**, 110 (1858).
[11] J. Am. Chem. Soc., **16**, 339 (1894).
[12] Ztschr. anorg. Chem., **19**, 101 (1899).

fair success, but their precipitates were somewhat colored, hence impure.

The explanation of how some barium sulphate is retained by solutions of iron salts and how iron salts are carried down by barium sulphate has been the subject of considerable work and speculation. Jannasch and Richards furnished some evidence for the existence of a barium ferric sulphate[1] in the impure precipitates before they were heated. On heating, sulphuric acid was lost and ferric oxide left behind in the barium sulphate. Ostwald[2] suggested an analogy between heated solutions containing iron sulphate and those containing chromium sulphate. In the latter case there is evidence of the existence of complex ions or groups, in the hot solutions, which do not yield $\overset{=}{SO_4}$ in the presence of $\overset{++}{Ba}$ ions. This analogy led Küster and Thiel to quite an elaborate study,[3] and to the assumption of the complex $(BaFe(SO_4)_2)_2$, as the form in which the iron enters the precipitates. Richards[4] took issue with them upon this point and upon the basis of Recoura's[5] and Whitney's[6] work on solutions of chromium salts as well as upon his own studies of "occlusion," favored the assumption of a basic complex, $Fe(SO_4)OH$. The results of Ostwald's suggestion are summed up in a statement to be found in Küster and Thiel's last article,[7] to the effect that it is impossible to decide what the complex is by the data at hand.

Schneider[8] has subjected the double salt idea[9] of Jannasch and Richards to an experimental test. The tenacity with which iron is retained by barium sulphate, even when treated with strong acids, suggested to Schneider that a barium ferric sulphate, if formed at all, must be very stable. So stable a salt should form with ease, and should form in larger and larger amounts, the more favorable the conditions for the contact of nascent barium sulphate with an excess of ferric sulphate. Schneider's experiments show, however, that when varying amounts of barium sulphate are precipitated in the presence of the same amount of iron and in the same volume of solution, after enough sulphuric acid is present to convert

[1] *Loc cit.*, p. 332.
[2] Ztschr. phys. Chem., **29**, 340.
[3] Ztschr. anorg. Chem., **22**, 424 (1900).
[4] *Ibid.*, **23**, 383 (1900).
[5] Ann. chim. phys., [7], **4**, 494.
[6] Ztschr. phys. Chem., **20**, 40; J. Am. Chem. Soc., **21**, 1075.
[7] Ztschr. anorg. Chem., **25**, 322 (1900).
[8] Ztschr. phys. Chem., **10**, 425 (1892).
[9] The idea of double salts to explain analogous difficulties with barium sulphate had been used by Turner (Phil. Trans., 1829, (4), p. 291) and Claus (J. prakt. Chem., **85**, 129 (1862)).

all the iron into neutral ferric sulphate, the percentage of iron in the precipitates becomes practically constant, with a value of about 1.24 per cent. Further the mass of ferric sulphate in the precipitates beyond this limit increases directly as the mass of barium sulphate. When a constant amount of barium sulphate is precipitated in the presence of varying amounts of iron in equal volumes of solution, experiment proves that an excess of ferric sulphate is without influence after the barium sulphate has once reached its maximum ability to retain iron. According to Schneider these experimental results clearly indicate that we have here to deal with a solid solution, the barium sulphate being able to dissolve ferric sulphate, but, like any other solvent, only able to dissolve it up to its own point of saturation—a perfectly constant proportion, no matter how great the excess of ferric sulphate present.

To one who has followed these matters carefully through the literature, either the '' Fresenius method'' or the '' Lunge method'' in the final form given it by Küster and Thiel, recommends itself as reliable for the determination of sulphur in the presence of iron. The '' zinc reduction method'' cannot be considered as trustworthy at present, and the '' organic acid method'' is unreliable. As to an explanation of the appearance of iron in barium sulphate precipitates, it seems unjustifiable to go beyond Schneider's conclusions until further experiments have been carried out.   D. W. HORN.

INDEX TO VOL. XXVII.

AUTHORS.

SUBJECTS.

FORMULAS.

C_1-GROUP.

1 II.

C_2-GROUP.

2 III.

2 IV.

C_3-GROUP.

3 III.

C_4-GROUP.

4 III.

4 IV.

4 V.

C$_5$-GROUP.

C$_6$-GROUP.

C$_7$-GROUP.

C$_8$-GROUP.

10 III.

10 IV.

C_{11}-GROUP.

11 III.

11 IV.

C_{12}-GROUP.

12 III.

12 IV.

C₁₃-GROUP.

13 IV.

13 V.

C₁₄-GROUP.

14 III.

14 IV.

C₁₅-GROUP.

15-IV.

C₁₆-GROUP.

16 IV.

C_{17}-GROUP.

C_{18}-GROUP.

18 III.

18 IV.

18 V.

C_{19}-GROUP.

C_{20}-GROUP.

C_{21}-GROUP.

21 IV.

C_{22}-GROUP.

22 IV.

22 V.

C_{24}-GROUP.

24 IV.

C_{26}-GROUP.

C_{28}-GROUP.

C_{32}-GROUP.

C_{34}-GROUP.

C_{36}-GROUP.

C_{42}-GROUP.